Chapter 7

Time-dependent Hamiltonians

So far, we have focused on approximating the eigenstates and eigenvalues of systems described by time-independent Hamiltonians. What happens when we can no longer neglect time dependence? We want to solve the equation:

$$i\frac{\partial}{\partial t}|\phi(t)\rangle = \hat{H}(t)|\phi(t)\rangle. \tag{7.1}$$

Equivalently, we can always write

$$|\phi(t)\rangle = \hat{U}(t,t_0)|\phi(t_0)\rangle. \tag{7.2}$$

for some unitary $\hat{U}(t,t_0)$. If the Hamiltonian is time-independent, it has the form

$$\hat{U}(t,t_0) = e^{-i\hat{H}(t-t_0)}, \tag{7.3}$$

but when there is explicit time dependence we cannot use this simple expression. This chapter will be give you some tools for computing the propagator in this case.

We will start by deriving something called the 'Dyson series'. This gives an exact expression for the evolution operator of a quantum system with a time dependent Hamiltonian. Unfortunately this expression is in most cases so disgustingly messy that you can not do much with it. We will then explore the interaction representation which (partially) simplifies the picture. Finally, we will go back to perturbation theory (this time 'time-dependent perturbation theory') to show that if the time dependent part of the Hamiltonian is only a small perturbation then calculations again become nice and tractable.

7.1 Dyson series

I warn you that this is a slightly fiddly derivation - but it's one of those derivations everyone needs to see at least once.

Plugging our expression for the evolution operator, Eq. (7.2), into the Schrodinger equation, Eq. (7.1), we have

$$i\frac{\partial}{\partial t}\hat{U}(t,t_0)|\phi(t_0)\rangle = \hat{H}(t)|\phi(t)\rangle. \tag{7.4}$$

As this holds for any state we thus have

$$\begin{cases} i\frac{\partial}{\partial t}\hat{U}(t,t_0) = \hat{H}(t)\hat{U}(t,t_0), \\ \hat{U}(t_0,t_0) = \mathbb{1}. \end{cases} \tag{7.5}$$

The exact time evolution operator in the case of a time dependent Hamiltonian is obtained by solving this system of equations. Integrating the first equation from t_0 to t gives:

$$\begin{aligned} i\int_{t_0}^{t} dt_1 \frac{\partial}{\partial t}\hat{U}(t_1,t_0) &= \int_{t_0}^{t} dt_1 \hat{H}(t_1)\hat{U}(t_1,t_0) \\ \Longrightarrow i\left(\hat{U}(t,t_0) - \mathbb{1}\right) &= \int_{t_0}^{t} dt_1 \hat{H}(t_1)\hat{U}(t_1,t_0). \end{aligned}$$

Therefore,

$$\begin{aligned} \hat{U}(t,t_0) &= \mathbb{1} - i\int_{t_0}^{t} dt_1 \hat{H}(t_1)\hat{U}(t_1,t_0) \\ &= \mathbb{1} - i\int_{t_0}^{t} dt_1 \hat{H}(t_1)\left(\mathbb{1} - i\int_{t_0}^{t_1} dt_2 \hat{H}(t_1)\hat{U}(t_2,t_0)\right) \\ &= \mathbb{1} - i\int_{t_0}^{t} dt_1 \hat{H}(t_1) + (-i)^2\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \hat{H}(t_1)\hat{H}(t_2)\hat{U}(t_2,t_0) \\ &= \mathbb{1} + \sum_{n=1}^{\infty}(-i)^n \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \cdots \int_{t_0}^{t_{n-1}} dt_n \hat{H}(t_1)\hat{H}(t_2)\hat{H}(t_3)\cdots\hat{H}(t_n) \end{aligned} \tag{7.6}$$

where $t_0 \le t_n \le t_{n-1} \le \cdots \le t_2 \le t_1 \le t$. (Note that the remainder term vanishes because the remainder term vanishes in the limit $n \to \infty$ hence $U(t_n, t_0)$ not appearing in the final line above.)

This looks pretty messy and hard to work with. In particular, its a pain how each of the integrals range depend on other parameters we are integrating over. It would be much nicer if all the integrals were between t_0 and t. To do so [1], we will need to introduce the *time ordering operator*, T. This is defined as follows:

$$T\left[H(t_1)H(t_2)\cdots H(t_n)\right] = H(t_{i_1})H(t_{i_2})\cdots H(t_{i_n}), \quad \text{where} \quad t_{i_1} > t_{i_2} > \cdots > t_{i_n}\,. \tag{7.7}$$

That is, the time-ordering operator tells you to reorder the operators so the time arguments of the corresponding operators *decrease* as you go from the left to the right. You end up with an expression where the largest time appears in the argument of the first (left most) operator and the smallest time appears in the argument of the last (right most) operator. For example, if $t_2 < t_1$ then you have

$$T(H(t_2)H(t_1)) = H(t_1)H(t_2)\,. \tag{7.8}$$

Ok, so how does this help to simplify Eq. (7.6)? To see how let's look at the term:

$$J_2 = \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \hat{H}(t_1)\hat{H}(t_2) \text{ with } t_2 \le t_1\,. \tag{7.9}$$

In this expression the integration over t_2 is performed first from t_0 to t_1, and then t_1 is integrated from t_0 to t. This represents all the pairs (t_1, t_2) where $t_2 \le t_1 \le t$. Geometrically, we can visualise this as looking for the area of the shaded area in Fig. 7.1(a). Now, as $t_2 \le t_1$ we have $T\left[H(t_1)H(t_2)\right] = H(t_1)H(t_2)$ and so we are free to insert T into the above integral to give

$$J_2 = \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 H(t_1)H(t_2) = \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 T\left[H(t_1)H(t_2)\right] \tag{7.10}$$

[1] In places here I am directly copying from these notes- you may prefer to go and read the original.

Next, we are free to change the order of integration (this is equivalent to integrating over the shaded region in Fig. 7.1(b) which is the same as the region in (a)). Thus we have

$$J_2 = \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 H(t_1)H(t_2) = \int_{t_0}^{t} dt_2 \int_{t_2}^{t} dt_1 H(t_1)H(t_2). \tag{7.11}$$

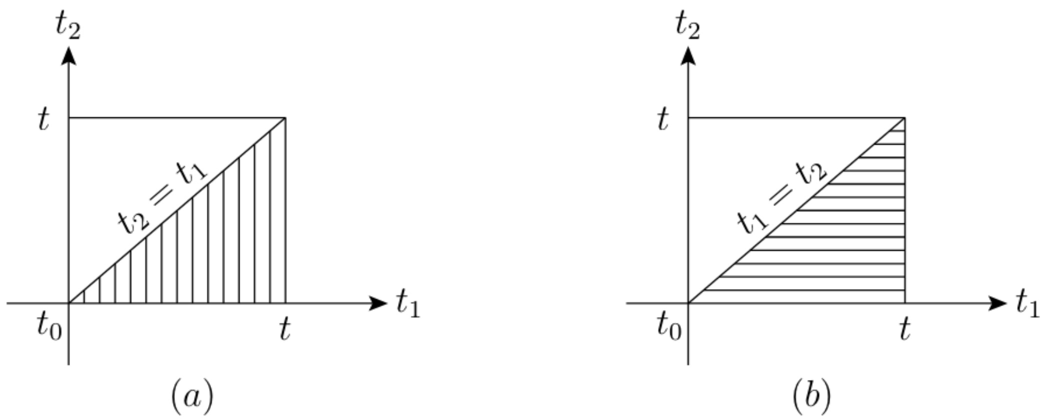

Figure 7.1: The integration region, $t_0 \le t_1 \le t$ and $t_0 \le t_2 \le t_1$, used in Eq. (7.10) (b) The integration region, $t_0 \le t_2 \le t$ and $t_2 \le t_1 \le t$, employed in Eq. (7.11) after interchanging the order of integration. (Image from this nice set of notes on the Dyson series.)

As the integration variables, t_1 and t_2, are dummy labels, we can relabel the integration variables in the final expression in Eq. (7.11) with by $t_1 \to t_2$ and $t_2 \to t_1$ to give:

$$J_2 = \int_{t_0}^{t} dt_1 \int_{t_1}^{t} dt_2 H(t_2)H(t_1) = \int_{t_0}^{t} dt_1 \int_{t_1}^{t} dt_2 T\left[H(t_1)H(t_2)\right]. \tag{7.12}$$

In the second equality we have inserted the T symbol. As now $t_2 \ge t_1$ (after the relabelling), in this case we have $T\left[H(t_1)H(t_2)\right] = H(t_2)H(t_1)$. That is, the integration region now consists of the area of the half square above the diagonal line shown in Fig. 7.1(a).

We now have two different expressions for J_2,

$$J_2 = \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 T\left[H(t_1)H(t_2)\right] = \int_{t_0}^{t} dt_1 \int_{t_1}^{t} dt_2 T\left[H(t_1)H(t_2)\right]. \tag{7.13}$$

Therefore, $2J_2$ is equal to the sum of the two integrals given in Eq. (7.13). By adding the two integrals, the dependence on the integration limit t_1 disappears. The integration region is now the area bounded by the full square. After dividing by two, we end up with,

$$J_2 = \frac{1}{2} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 T\left[H(t_1)H(t_2)\right]. \tag{28}$$

That is, we have successfully decoupled the limits.

Iterating this procedure, you find that the time evolution operator can be written in the form:

$$\hat{U}(t,t_0) = \mathbb{1} + \sum_{n=1}^{\infty} (-i)^n \frac{1}{n!} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \cdots \int_{t_0}^{t} dt_n \hat{T}\left(\hat{H}(t_1)\cdots\hat{H}(t_n)\right). \tag{7.14}$$

Note the presence of the corrective factor $\frac{1}{n!}$ due to the fact that the integral over each of the $n!$ possible combinations of the positions of t_i remains the same because the operator $\hat{T}$ always rearranges the t_i in such a way that they return to their initial positions. It is customary to condense the expression 7.14 into the form:

$$\hat{U}(t,t_0) = \hat{T}\left(e^{-i\int_{t_0}^{t} dt_1 \hat{H}(t_1)}\right). \tag{7.15}$$

Note 7.1.1. 1. If the Hamiltonian $\hat{H}$ is independent of time, then clearly $[\hat{H}(t_i), \hat{H}(t_j)] = 0$ for all t_i, t_j. As such, the operator $\hat{T}$ acts trivially on the product of Hamiltonians. So we have:

$$\begin{aligned}\hat{U}(t,t_0) &= \mathbb{1} + \sum_{n=1}^{\infty} (-i)^n \frac{1}{n!} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \cdots \int_{t_0}^{t} dt_n \hat{T}\left(\hat{H}(t_1)\cdots\hat{H}(t_n)\right) \\ &= \mathbb{1} + \sum_{n=1}^{\infty} (-i)^n \frac{1}{n!} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \cdots \int_{t_0}^{t} dt_n \hat{H}(t_1) \cdots \hat{H}(t_n),\end{aligned}$$

which, in exponential notation, gives $\hat{U}(t,t_0) = e^{-i\int_{t_0}^{t} dt_1 \hat{H}(t_1)}$. Moreover, since $\hat{H}$ is independent of time, $\int_{t_0}^{t} dt' \hat{H}(t') = \hat{H}(t - t_0)$, and the time evolution operator can be rewritten as $\hat{U}(t,t_0) = \left(e^{-i\hat{H}(t-t_0)}\right)$. As such we indeed recover the standard expression for the evolution under a time independent Hamiltonian (Eq.(7.3)).

2. In general, there is no guarantee that $\hat{T}\left(e^{-i\int_{t_0}^{t} dt_1 \hat{H}(t_1)}\right) = e^{-i\int_{t_0}^{t} dt_1 \hat{H}(t_1)}$. Therefore, you have to go back to the uncompressed expression 7.14 for $\hat{U}$ and explicitly compute each term of the expansion before summing them. This is generally pretty painful unless you get lucky and a recurrence relation between all the terms is found. Therefore, we usually focus on situations where we can limit the expansion to a few terms.

3. In the context of quantum computing it is common to attempt to approximate $\hat{U}(t,t_0)$ by breaking the continuous time evolution down into discrete time steps and use:

$$\hat{U}(t,t_0) \approx \prod_j e^{-i\hat{H}(t_j)\delta t} := \hat{U}_{\text{disc}}(t,t_0).$$

where $\delta t = t/m_t$ for some integer m_t. It can be shown that the resulting approximation is upper bounded by

$$\left\| \int_{t_0}^{t} ds \hat{H}(s) - \delta t \sum_{r=1}^{m_t} \hat{H}(t_0 + r\delta t) \right\|^2 \tag{7.16}$$

where $||...||$ is any matrix norm that is unitarily invariant. The key thing to understand about this approximation is that you are effectively breaking the continuous evolution of the Hamiltonian down into discrete time blocks and assuming that each block (approximately) commutes.

7.2 Interaction Representation

You are already familiar with the formalism of quantum mechanics from the Heisenberg and Schrödinger perspectives. In this section, we introduce a new representation called the *interaction representation*.

Let's begin with some reminders:

1. In the Schrödinger representation, it is the states $|\phi_S(t)\rangle$ that explicitly depend on time. The evolution is governed by the following equation:

$$i\frac{\partial}{\partial t}|\phi_S(t)\rangle = \hat{H}(t)|\phi_S(t)\rangle .$$

   In this representation, observables are fixed operators, and any time dependence they have, if at all, is intrinsic and not governed by $\hat{H}$.

2. In the Heisenberg viewpoint, the time dependence is instead transferred to the operators. The state vectors are assumed to be fixed, and their time dependence is intrinsic. The system's time evolution is governed by:

$$\begin{cases} |\phi_H(t)\rangle = |\phi_S(t_0)\rangle , \\ \hat{O}_H(t) = \hat{U}_S^\dagger(t,t_0)\hat{O}_S(t)\hat{U}_S(t,t_0) \end{cases}$$

3. These two definitions lead to identical expectation values:

$$\begin{aligned} \left\langle \phi_H(t) \middle| \hat{O}_H(t) \middle| \phi_H(t) \right\rangle &= \left\langle \phi_H(t) \middle| \hat{U}_S^\dagger(t,t_0)\hat{O}_S(t)\hat{U}_S(t,t_0) \middle| \phi_H(t) \right\rangle \\ &= \left\langle \hat{U}_S^\dagger(t,t_0)\phi_S(t) \middle| \hat{U}_S^\dagger(t,t_0)\hat{O}_S(t)\hat{U}_S(t,t_0) \middle| \hat{U}_S^\dagger(t,t_0)\phi_S(t) \right\rangle \\ &= \left\langle \hat{U}_S(t,t_0)\hat{U}_S^\dagger(t,t_0)\phi_S(t) \middle| \hat{O}_S(t) \middle| \hat{U}_S(t,t_0)\hat{U}_S^\dagger(t,t_0)\phi_S(t) \right\rangle \\ &= \left\langle \phi_S(t) \middle| \hat{O}_S(t) \middle| \phi_S(t) \right\rangle . \end{aligned}$$

   In other words, both representations lead to the same physics and we are free to pick which ever one makes our calculations easiest.

The interaction representation is a kind of "blend" of these two points of view. We start with a problem described by a Hamiltonian of the form:

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t).$$

We will treat the time dependence due to the perturbation $\hat{V}$ as evolving the states (Schrodinger-style) and the time dependence due to $\hat{H}_0$ as evolving the observables (Heisenberg-style).

Let us start by defining the evolution of states and operators in the interaction picture as:

$$\begin{cases} \hat{O}_I(t) = e^{i\hat{H}_0(t-t_0)}\hat{O}_S(t)e^{-i\hat{H}_0(t-t_0)}, \\ |\phi_I(t)\rangle = e^{i\hat{H}_0(t-t_0)}|\phi_S(t)\rangle = e^{i\hat{H}_0(t-t_0)}\hat{U}_S(t,t_0)|\phi_S(t_0)\rangle . \end{cases} \tag{7.17}$$

It is straightforward to check that this is consistent with the Schrodinger picture as:

$$\begin{aligned} \left\langle \phi_I(t) \middle| \hat{O}_I(t) \middle| \phi_I(t) \right\rangle &= \langle \phi_S(t)| e^{-i\hat{H}_0(t-t_0)}e^{i\hat{H}_0(t-t_0)}\hat{O}_S(t)e^{-i\hat{H}_0(t-t_0)}e^{i\hat{H}_0(t-t_0)}|\phi_S(t)\rangle \\ &= \left\langle \phi_S(t) \middle| \hat{O}_S(t) \middle| \phi_S(t) \right\rangle . \end{aligned} \tag{7.18}$$

If this seems a little arbitrary and pointless currently, don't worry, it will hopefully become clearer in a bit while it is useful. But before we get there let's keep going with seeing how this representation works.

We can implicitly define the interaction evolution operator $\hat{U}_I(t,t_0)$ as:

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

Figure 7.2: I had no idea what is meant to be going on in this meme when I first saw it and just thought it would just make this page a little more colourful. Then someone sent me this link and I realised it was a half-decent explanation of the interaction picture. Credit: L'heure est grave.

This, combined with the second equation in (7.17), gives us an explicit expression for $\hat{U}_I(t,t_0)$:

$$\hat{U}_I(t,t_0) = e^{i\hat{H}_0(t-t_0)}\hat{U}_S(t,t_0). \tag{7.19}$$

Let's now have a look at how such an operator evolves. Differentiating it gives:

$$\begin{aligned}
\frac{\partial}{\partial t}\hat{U}_I(t,t_0) &= e^{i\hat{H}_0(t-t_0)}i\hat{H}_0\hat{U}_S(t,t_0) - ie^{i\hat{H}_0(t-t_0)}\hat{H}(t)\hat{U}_S(t,t_0)\\
&= -ie^{i\hat{H}_0(t-t_0)}\left(\hat{H}(t)-\hat{H}_0\right)\hat{U}_S(t,t_0)\\
&= -ie^{i\hat{H}_0(t-t_0)}\hat{V}(t)\hat{U}_S(t,t_0)\\
&= -ie^{i\hat{H}_0(t-t_0)}\hat{V}(t)e^{-i\hat{H}_0(t-t_0)}e^{i\hat{H}_0(t-t_0)}\hat{U}_S(t,t_0)\\
&= -i\hat{V}_I(t)\hat{U}_I(t,t_0).
\end{aligned}$$

where in the final line we use the definition of an operator in the interaction picture from Eq.(7.17). Thus we have that the analogue of the Schrodinger equation for the evolution operator in the interaction picture is given by:

$$i\frac{\partial}{\partial t}\hat{U}_I(t,t_0) = \hat{V}_I(t)\hat{U}_I(t,t_0). \tag{7.20}$$

The key thing to notice is that in the equation that governs the evolution of the evolution operator in the interaction picture, i.e., Eq. (7.20), it is the perturbation that plays the role of the Hamiltonian! That is, we have simplified the differential equation we need to solve to find the propagator by hiding $\hat{H}_0$. If we push the analogy a bit further, we can use similar reasoning as we used to find the propagator in the Schrodinger picture, to obtain an expansion of $\hat{U}_I(t,t_0)$:

$$\begin{aligned}
\hat{U}_I(t,t_0) &= \mathbb{1} + \sum_{i=1}^{\infty}(-i)^n\int_{t_0}^{t}dt_1\int_{t_0}^{t}dt_2\cdots\int_{t_0}^{t}dt_n\left(\hat{V}_I(t_1)\cdots\hat{V}_I(t_{n-1})\right)\\
&= \mathbb{1} + \sum_{i=1}^{\infty}(-i)^n\frac{1}{n!}\int_{t_0}^{t}dt_1\int_{t_0}^{t}dt_2\cdots\int_{t_0}^{t}dt_n\hat{T}\left(\hat{V}_I(t_1)\cdots\hat{V}_I(t_n-1)\right),
\end{aligned} \tag{7.21}$$

which, similarly to before, we can also put in a more condensed version:

$$\hat{U}_I(t,t_0) = \hat{T}\left(e^{-i\int_{t_0}^{t} dt'\hat{V}_I(t')}\right).$$

As mentioned earlier, such an expansion is only meaningful if it is possible to truncate the sum from a certain term onwards. This is feasible when $\hat{V}(t)$ is a small perturbation.

7.3 Transition Probabilities

Consider a system described by a Hamiltonian of the form

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t) \tag{7.22}$$

where

$$\hat{V} = \begin{cases} 0 \text{ if } t \le t_0 \\ \hat{V}(t) \text{ if } t > t_0. \end{cases} \tag{7.23}$$

We will use $|n\rangle$ and E_n to denote the states and eigenvalues of the unperturbed Hamiltonian. Suppose the system is in the eigenstate $|i\rangle$ at $t = t_0$, so its temporal evolution is determined by:

$$|\phi_S(t)\rangle = U_S(t,t_0)\,|i\rangle = \sum_{n=0}^{\infty} c_n(t)\,|n\rangle\,,$$

where $\sum_{n=0}^{\infty}|c_n|^2 = 1$. Since the states $|n\rangle$ are orthonormal, projecting the state $|\phi_S\rangle$ onto the state $|n\rangle$ determines the coefficient c_n, and this holds for any $n \in \mathbb{N}$:

$$\begin{aligned} c_n(t) = \langle n|\phi_S(t)\rangle &= \langle n|\hat{U}_S(t,t_0)|i\rangle \\ &= \langle n|\, e^{-i\hat{H}_0(t-t_0)}\hat{U}_I(t,t_0)\,|i\rangle \\ &= e^{-i\frac{E_n(t-t_0)}{\hbar}}\,\langle n|\hat{U}_I(t,t_0)|i\rangle\,. \end{aligned}$$

The amplitude $c_n(t)$ is simply the amplitude to find the system in eigenstate $|n\rangle$ given that it started in state $|i\rangle$. Thus the transition probability $P_{i\to n}$ from the initial state $|i\rangle$ to any eigenstate $|n\rangle$ of $\hat{H}_0$ is simply the mod-square of this:

$$P_{i\to n} = |\langle n|\phi_S(t)\rangle|^2 = |c_n(t)|^2 = \left|\langle n|\hat{U}_I(t,t_0)|i\rangle\right|^2.$$

Note that by assumption $\hat{V}(t) = 0$ for all $t \le t_0$, so $|i\rangle$ is not only an eigenstate of $\hat{H}_0$ but also of $\hat{H}$ for $t \le t_0$. Let's determine the expression of the transition probability at the first order in $\hat{V}$. Note that (from Eq. (7.21)) in the first order in V the propagator is of the form:

$$\hat{U}_I(t,t_0) = \mathbb{1} - i\int_{t_0}^{t} dt_1 \hat{V}_I(t_1),$$

and so (assuming $n \ne i$) we have

$$\begin{aligned} \langle n|\hat{U}_I(t,t_0)|i\rangle &= -i\int_0^t dt_1\,\langle n|\hat{V}_I(t,t_0)|i\rangle \\ &= -i\int_{t_0}^{t} dt_1\,\langle n|e^{i\hat{H}_0(t_1-t_0)}\hat{V}(t_1,t_0)e^{-i\hat{H}_0(t_1-t_0)}|i\rangle \\ &= -i\int_{t_0}^{t} dt_1 e^{-i(E_n-E_i)(t_1-t_0)}\,\langle n|\hat{V}(t,t_0)|i\rangle\,, \end{aligned}$$

and finally

$$P_{i\to n} = \left| -i \int_{t_0}^{t} dt_1 e^{-i(E_n - E_i)(t_1 - t_0)} \langle n|\hat{V}(t_1, t_0)|i\rangle \right|^2 . \tag{7.24}$$

This is the first-order time-dependent perturbation theory expression for the computation of a transition probability. Let's now evaluate it for some common cases of interest.

Turning on a constant perturbation. Let's consider the special case where the potential (once turned on) does not depend on time. That is, let's suppose that

$$\hat{V} = \begin{cases} 0 \text{ if } t \le t_0 \\ \hat{V} \text{ if } t > t_0, \end{cases}$$

and 7.24 becomes:

$$\begin{aligned} P_{i\to n}(t) &= \left| \langle n|\hat{V}|i\rangle \int_{t_0}^{t} dt_1 e^{-i(E_n - E_i)(t_1 - t_0)} \right|^2 \\ &= \left| \frac{1}{i} \langle n|\hat{V}|i\rangle \frac{e^{-i(E_n - E_i)(t - t_0)} - 1}{E_n - E_i} \right|^2 \\ &= \left| \langle n|\hat{V}|i\rangle \right|^2 \frac{4}{(E_n - E_i)^2} \sin^2\left(\frac{(E_n - E_i)(t - t_0)}{2} \right). \end{aligned}$$

Without loss of generality we can take $t_0 = 0$ and rewrite our expression for $P_{i\to n}(t)$ as

$$P_{i\to n}(t) = \left| \langle n|\hat{V}|i\rangle \right|^2 f\left(E_n - E_i\right), \tag{7.25}$$

with $f(\omega) = \frac{4}{\omega^2} \sin\left(\frac{\omega t}{2}\right)$ and $\omega = E_n - E_i$. The function $f(\omega)$ is sketched in Fig. 7.3. Note that:

$$f(\omega) = \begin{cases} 0 \text{ for } \frac{\omega t}{2} = k\pi \\ \\ \frac{4}{\omega^2} \text{ if } \frac{\omega t}{2} = \frac{\pi}{2} + k\pi, \end{cases}$$

where k is an integer. Thus we see that at a fixed time t, the probability of transitioning to a state $|n\rangle$ will be highest for those such that $\omega = E_n - E_i$ satisfies $\omega \le \frac{2\pi}{t}$.

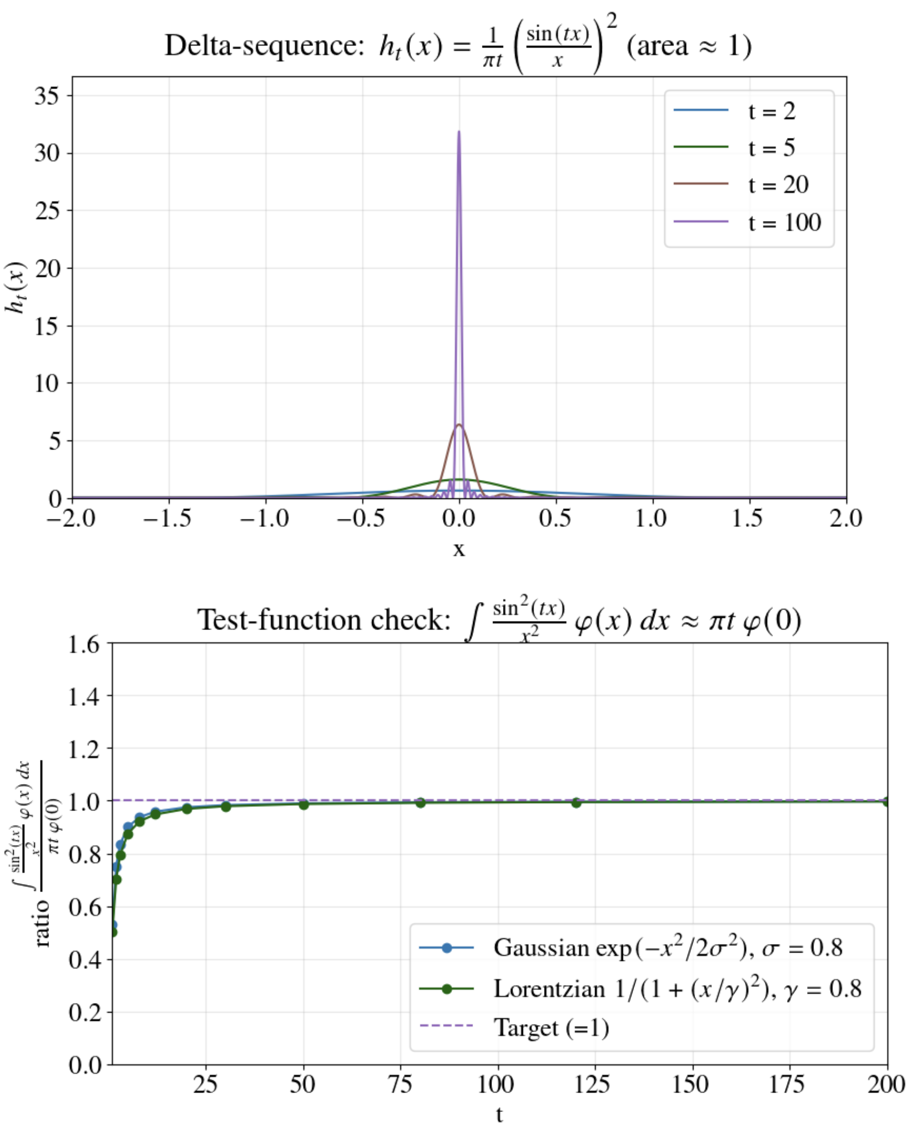

Figure 7.3: **Top:** The functions $h_t(x) = \frac{1}{\pi t}\left(\frac{\sin(tx)}{x}\right)^2$ form a delta sequence: as t increases, the peak around $x = 0$ becomes narrower (characteristic width $\sim 1/t$) and taller (peak height $h_t(0) = t/\pi$) while the total area remains unity, so h_t converges to $\delta(x)$ in the distributional sense. **Bottom:** Numerical distributional check of the Golden Rule approximation. For several smooth test functions $\varphi(x)$ (Gaussian, Lorentzian, each normalised so that $\varphi(0) = 1$), we plot the ratio $\left[\int_{-L}^{L}(\sin^2(tx)/x^2)\,\varphi(x)\,dx\right]/[\pi t\,\varphi(0)]$ versus t. The ratio approaches 1 as t grows, illustrating that $\sin^2(tx)/x^2$ acts like $\pi t\,\delta(x)$ when integrated against slowly varying functions.

We now do something which is standard in physics textbook derivations but would make a mathematician cry [2] and say

$$\lim_{t\to\infty} \frac{\sin^2(xt)}{x^2} = \pi t \delta(x). \tag{7.26}$$

The way to understand this statement is to say that in the limit of large t we have that

$$\frac{\sin^2(xt)}{x^2} \approx \pi t \delta(x)\,. \tag{7.27}$$

[2]The discussion here might also make you feel a bit better.

That is, the leading contribution in the limit of large t scales as πt if $x = 0$ but otherwise is approximately 0.

We thus obtain the *Fermi golden rule*:

$$\lim_{t\to\infty} P_{i\to n}(t) = 4\left|\langle n|\hat{V}|i\rangle\right|^2 \lim_{t\to\infty}\frac{1}{\omega^2}\sin^2\left(\frac{\omega t}{2}\right) = 2\pi t\left|\langle n|\hat{V}|i\rangle\right|^2 \delta(E_n - E_i) \tag{7.28}$$

where the final line we use $\omega = E_n - E_i$.

It is sometimes more useful to work with a *transition probability per unit time*, in this case we have

$$\frac{\partial P_{i\to n}(t)}{\partial t} = 2\pi\left|\langle n|\hat{V}|i\rangle\right|^2 \delta(E_n - E_i)\,. \tag{7.29}$$

Oscillatory potential. Let's suppose now that the potential is given by

$$\hat{V} = \begin{cases} 0 \text{ if } t \le t_0 \\ \hat{V}(t)e^{i\omega t} + \hat{V}^\dagger e^{-i\omega t} \text{ if } t > t_0. \end{cases} \tag{7.30}$$

From Eq.(7.24), the equation for the transition probability is now given by:

$$\begin{aligned} P_{i\to n} &= \left|-i\int_0^t dt_1 e^{i(E_n-E_i)t_1}\left(\langle n|\hat{V}|i\rangle\, e^{i\omega t_1} + \langle n|\hat{V}^\dagger|i\rangle\, e^{-i\omega t_1}\right)\right|^2 \\ &= \left|\frac{1-e^{-i((E_n-E_i)+\omega)t}}{E_n - E_i + \omega}\langle n|\hat{V}|i\rangle + \frac{1-e^{-i((E_n-E_i)-\omega)t}}{E_n - E_i - \omega}\langle n|\hat{V}^\dagger|i\rangle\right|^2. \end{aligned}$$

At long times, transitions to energy states with $E_n = E_i \pm \omega$ are favoured, and (via a similar analysis to above) we find:

$$\omega_{i\to n}(t) = 2\pi\left|\langle n|\hat{V}|i\rangle\right|^2 \delta(E_n - E_i + \omega) + 2\pi\left|\langle n|\hat{V}^\dagger|i\rangle\right|^2 \delta(E_n - E_i - \omega).$$

Notice that the first term in the sum corresponds to an energy loss by the system, while the second term represents an energy gain by the system. This variant of Fermi's golden rule is very important, as it explains how optical transitions occur in the presence of an oscillating external electromagnetic field, for instance, between levels of an atom or a solid due to application of laser light.

Nearly constant perturbation. Let's now consider the case of a nearly constant perturbation

$$\hat{V}(t) = \hat{V}e^{\epsilon t}$$

where ϵ is real and positive. Instead of turning on the perturbation at time t_0, we here assume that it turns on very slowly from $t = -\infty$. We will take the limit $\epsilon \to 0$ at the end of the calculation to describe a constant perturbation.

Let's write the perturbative expansion of $\hat{U}_I(t, -\infty)$. For the sake of simplicity, which will become clear later, we will use the first form for the propagator obtained before the introduction of the time-ordered operator (i.e. Eq. (7.6) but with $\hat{H} \to \hat{V}_I$):

$$\hat{U}_I(t, -\infty) = \hat{I} - i\int_{-\infty}^{t} dt_1 \hat{V}_I(t_1) - \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \hat{V}_I(t_1)\hat{V}_I(t_2) + \cdots. \tag{7.31}$$

Let's now look at the transition amplitude:

$$c_n(t) = e^{-iE_n t}\langle n|\hat{U}_I(t,t_0)|i\rangle \tag{7.32}$$

where we have omitted the constant phase $e^{iE_n t_0}$. Combining the previous two equations and now keeping terms to *second order* in $\hat{V}_I$ gives:

$$e^{iE_n t}c_n(t) = \underbrace{-i\int_{-\infty}^{t} dt_1\,\langle n|\hat{V}_I(t_1)|i\rangle}_{I_1} - \underbrace{\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2\,\langle n|\hat{V}_I(t_1)\hat{V}_I(t_2)|i\rangle}_{I_2}$$

Let's start with the first integral. The calculation here proceeds in the same manner as for a constant and oscillatory perturbations. First we recall that

$$\begin{aligned}\hat{V}_I(t) &= e^{i\hat{H}_0 t}\hat{V}(t)e^{-i\hat{H}_0 t\hbar}\\ &= e^{i\hat{H}_0 t}\hat{V}e^{\epsilon t}e^{-i\hat{H}_0 t\hbar}\end{aligned}$$

Using the properties of the eigenstate we then have:

$$\begin{aligned}I_1 &= \int_{-\infty}^{t} dt_1\,\langle n|\hat{V}_I(t_1)|i\rangle = \langle n|\hat{V}|i\rangle \int_{-\infty}^{t} dt_1 e^{i[(E_n-E_i)t_1 - i\epsilon t_1]}\\ &= \langle n|\hat{V}|i\rangle \left.\frac{\exp\left(i((E_n-E_i)t_1 - i\epsilon t_1)\right)}{i(E_n-E_i-i\epsilon)}\right|_{-\infty}^{t}\end{aligned}$$

If we were to stop at the first order, we would find the golden rule as follows:

$$P_{i\to n} = |c_n(t)|^2 = |\langle n|\hat{V}|i\rangle|^2 \frac{e^{2\epsilon t}}{(E_n-E_i)^2+\epsilon^2}$$

and so

$$\omega_{i\to n} = \frac{dP_{i\to n}}{dt} = |\langle n|\hat{V}|i\rangle|^2 \frac{2\epsilon e^{2\epsilon t}}{(E_n-E_i)^2+\epsilon^2} \tag{7.33}$$

Let's check that our result here agrees with that obtained for the constant perturbation in the limit that $\epsilon \to 0$. To do so we first note that

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

and thus

$$\lim_{\epsilon\to 0}\frac{dP_{i\to n}}{dt} = 2\pi|\langle n|\hat{V}|i\rangle|^2\delta(E_n-E_i)\,. \tag{7.34}$$

That is, we find we do indeed regain the previous result in Eq. (7.29).

But what about to second order? Let's now calculate I_2:

$$I_2 = \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \sum_m \langle n|\hat{V}_I(t_1)|m\rangle\langle m|\hat{V}_I(t_2)|i\rangle$$

where we have introduced $\hat{I}$ as $\sum_m |m\rangle\langle m|$

$$\begin{aligned}
I_2 &= \sum_m \langle n|\hat{V}|m\rangle \langle m|\hat{V}|i\rangle \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \exp\left(i(E_n - E_m - i\epsilon)t_1\right) \exp\left(i(E_m - E_i - i\epsilon)t_2\right) \\
&= \sum_m \langle n|\hat{V}|m\rangle \langle m|\hat{V}|i\rangle \int_{-\infty}^{t} dt_1 \exp\left(i(E_n - E_m - i\epsilon)t_1\right) \left. \frac{\exp\left(i(E_m - E_i - i\epsilon)t_2\right)}{i(E_m - E_i - i\epsilon)} \right|_{-\infty}^{t_1} \\
&= \sum_m \langle n|\hat{V}|m\rangle \langle m|\hat{V}|i\rangle \int_{-\infty}^{t} dt_1 \exp\left(i(E_n - E_m - i\epsilon)t_1\right) \frac{\exp\left(i(E_m - E_i - i\epsilon)t_1\right)}{i(E_m - E_i - i\epsilon)} \\
&= -\sum_m \frac{\langle n|\hat{V}|m\rangle \langle m|\hat{V}|i\rangle \exp\left(i(E_n - E_i - 2i\epsilon)t\right)}{(E_m - E_i - i\epsilon)(E_n - E_i - 2i\epsilon)}
\end{aligned}$$

The term $\exp\left(i(E_n - E_i - 2i\epsilon)t\right)/(E_n - E_i - 2i\epsilon)$ is the same as in I_1 (except for $\epsilon \to 2\epsilon$, which doesn't change anything in the limit $\epsilon \to 0$). If we start from

$$\exp\left(iE_n t\right) c_n(t) = \hat{I} - i\int_{-\infty}^{t} dt_1 \hat{V}_I(t_1) - 1\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \hat{V}_I(t_1)\hat{V}_I(t_2)$$

and replace the two previous results, we have

$$\begin{aligned}
P_{i\to n} = |c_t(t)|^2 &= \left| i\int_{-\infty}^{t} dt_1 \hat{V}_I(t_1) + 1\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} \hat{V}_I(t_1)\hat{V}_I(t_2) \right|^2 \\
&= \left| \langle n|\hat{V}|i\rangle + \sum_m \frac{\langle n|\hat{V}|m\rangle \langle m|\hat{V}|i\rangle}{E_m - E_i - i\epsilon} \right|^2 \frac{e^{2\epsilon t}}{(E_n - E_i)^2 + \epsilon^2}
\end{aligned}$$

and

$$\lim_{\epsilon\to 0} \frac{dP_{i\to n}}{dt} = \omega_{i\to n} = 2\pi \left| \langle n|\hat{V}|i\rangle + \sum_m \frac{\langle n|\hat{V}|m\rangle \langle m|\hat{V}|i\rangle}{E_m - E_i - i0^+} \right|^2 \delta(E_n - E_i)$$

which is the second-order transition rate for a time-independent perturbation $\hat{V}$. Note the sum over intermediate states $|m\rangle$ typical of second-order perturbation. Here, a very suggestive image is that the system undergoes "virtual" transitions to states $|m\rangle$ without conserving energy since they occur in an arbitrarily short time before going to state $|n\rangle$.