Week 8

PHY 304 Quantum Mechanics-II

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9 Quantum dynamics

So far we have encountered only two approaches to time-dependence (="dynamics") in quantum mechanics: (i) If the Hamiltonian itself is time-independent, we had already seen in Eq. (1.70) that once we solve the TISE (1.62), we actually also know the time dependence of the wavefunction and hence all physical observables. (ii) In a few examples such as example 1 and example 21, we had seen some brute force numerical solution of the TDSE (3.8), also for cases where the Hamiltonian is time-dependent.

We now attempt to understand different types of quantum dynamics also analytically from Eq. (3.8), for more insight than the computer can provide, and for case where numerical approaches are not practical or not powerful enough.

9.1 First order time-dependent perturbation theory

Further reading: For this section (Time-dependent perturbation theory), please also refer to Shankar, section 18 (SH)

Suppose our Hamiltonian is

$$\hat{H} = \hat{H}^{(0)} + \hat{H}'(t), \tag{9.1}$$

where the unperturbed Hamiltonian $\hat{H}^{(0)}$ does not depend on time and we assume we know all eigenstates and energies from $\hat{H}^{(0)}|\,\phi_n^{(0)}\,\rangle = E^{(0)}|\,\phi_n^{(0)}\,\rangle$. The perturbation $\hat{H}'(t)$ is somehow "small" and time-dependent. This is thus the same starting point as (7.1), except that we made the perturbation time-dependent (and skipped the placeholder λ used earlier to indicate "smallness").

If there was no perturbation, we can use (1.70) as in point (i) above to write the solution of the TISE as:

$$|\,\Psi^{(0)}(t)\,\rangle = \sum_n \underbrace{c_n(0)e^{-iE_n^{(0)}t/\hbar}}_{c_n(t)^{(0)}}|\,\phi_n^{(0)}\,\rangle. \tag{9.2}$$

Note, that in this, the probability p_k for the system to be found with energy $E_k^{(0)}$ upon a measurement remains constant:

$$p_k = |c_n(t)^{(0)}|^2 = |c_n(0)e^{-iE_n^{(0)}t/\hbar}|\,\phi_n^{(0)}\,\rangle|^2 = |c_n(0)|^2. \tag{9.3}$$

We say that the system cannot make a transition between two energy eigenstates n and n'. We will now see that this does not remain true, once we switch on the perturbation (see e.g. example 21).

9.1.1 Transition amplitudes

While Eq. (9.2) requires in an essential way that the Hamiltonian does not depend on time, even if the total Hamiltonian is time-dependent, we can still use the eigenstates of the unperturbed and time-independent Hamiltonian as a basis at each moment t in time, and thus write the total state as

$$|\,\Psi(t)\,\rangle = \sum_n \tilde{c}_n(t)|\,\phi_n^{(0)}\,\rangle, \tag{9.4}$$

where the coefficients $\tilde{c}_n(t)$ are now not equal to the $\tilde{c}_n(t)^{(0)}$ above. A typical mission statement for perturbation theory is now the following: Suppose the system is in some initial state i at the beginning: $|\,\Psi(0)\,\rangle = |\,\phi_i^{(0)}\,\rangle$ (hence $c_n(0) = \delta_{ni}$), what is the probability that it makes a transition to some final state f by the time t? This probability is given by $|\langle\,\phi_f^{(0)}\,|\,\Psi(t)\,\rangle|^2 = |\tilde{c}_f(t)|^2$.

To find $\tilde{c}(t)$, let us be guided by the fact that they become the $c_n(t)^{(0)}$ if $\hat{H}' = 0$ and write

$$|\,\Psi(t)\,\rangle = \sum_n d_n(t)e^{-iE_n^{(0)}t/\hbar}|\,\phi_n^{(0)}\,\rangle, \tag{9.5}$$

instead of (9.4) (this just defines some new coefficients $d_n(t)$ instead of $\tilde{c}_n(t)$. We now insert (9.5) into the TDSE (3.8) to reach

$$i\hbar\frac{d}{dt}\left[\sum_n d_n(t)e^{-iE_n^{(0)}t/\hbar}|\,\phi_n^{(0)}\,\rangle\right] = \left(\hat{H}^{(0)} + \hat{H}'(t)\right)\left[\sum_n d_n(t)e^{-iE_n^{(0)}t/\hbar}|\,\phi_n^{(0)}\,\rangle\right] \Leftrightarrow$$

$$i\hbar\sum_n\left[\dot{d}_n(t)e^{-iE_n^{(0)}t/\hbar} - \frac{iE_n^{(0)}t}{\hbar}d_n(t)e^{-iE_n^{(0)}t/\hbar}\right]|\,\phi_n^{(0)}\,\rangle = \left[\sum_n d_n(t)e^{-iE_n^{(0)}t/\hbar}\underbrace{\hat{H}^{(0)}|\,\phi_n^{(0)}\,\rangle}_{=E_n^{(0)}|\,\phi_n^{(0)}\,\rangle}\right]$$
$$+\sum_n d_n(t)e^{-iE_n^{(0)}t/\hbar}\hat{H}'(t)|\,\phi_n^{(0)}\,\rangle. \tag{9.6}$$

We now take the scalar product with $\langle\,\phi_f^{(0)}\,|$ since we are interested in $\tilde{c}_f(t)$ (and hence $d_f(t)$):

$$i\hbar\left[\dot{d}_f(t)e^{-iE_f^{(0)}t/\hbar} - \frac{iE_f^{(0)}t}{\hbar}d_f(t)e^{-iE_f^{(0)}t/\hbar}\right] = d_f(t)e^{-iE_f^{(0)}t/\hbar}E_f^{(0)} + \sum_n d_n(t)e^{-iE_n^{(0)}t/\hbar}\langle\,\phi_f^{(0)}\,|\hat{H}'(t)|\,\phi_n^{(0)}\,\rangle. \tag{9.7}$$

The second term on the left and first term on the right cancel, and the rest can be divided by some clutter to reach:

$$\dot{d}_f(t) = -\frac{i}{\hbar}\sum_n d_n(t) e^{i(E_f^{(0)}-E_n^{(0)})t/\hbar}\langle\, \phi_f^{(0)}\,|\hat{H}'(t)|\,\phi_n^{(0)}\,\rangle. \tag{9.8}$$

So far, we have not made any approximations. Now we apply perturbation theory.
Zeroth order: To zeroth order we neglect everything involving $\hat{H}'(t)$, thus (9.8) becomes $\dot{d}_f(t) = 0$, implying $d_f(t) = d_f(0) = c_f(0) = \delta_{if}$. The last step is because we started by saying the system is in the initial state i.
First order: Since the right hand side is already of order $\hat{H}'$, if we want to find the LHS to first order in $\hat{H}'$, the coefficient $d_n(t)$ can only contain the zeroth order result, hence:

$$\dot{d}_f(t) = -\frac{i}{\hbar}\sum_n \delta_{ni} e^{i(E_f^{(0)}-E_n^{(0)})t/\hbar}\langle\, \phi_f^{(0)}\,|\hat{H}'(t)|\,\phi_n^{(0)}\,\rangle = -\frac{i}{\hbar}e^{i(E_f^{(0)}-E_i^{(0)})t/\hbar}\langle\, \phi_f^{(0)}\,|\hat{H}'(t)|\,\phi_i^{(0)}\,\rangle, \tag{9.9}$$

which we can formally solve with initial condition $d_f(0) = \delta_{fi}$ to find the

Transition amplitude between two states in first order time-dependent perturbation theory as

$$d_f(t) = \delta_{fi} - \frac{i}{\hbar}\int_0^t dt'\; e^{i(E_f^{(0)}-E_i^{(0)})t'/\hbar}\langle\, \phi_f^{(0)}\,|\hat{H}'(t')|\,\phi_i^{(0)}\,\rangle \tag{9.10}$$

with transition probability $p_f(t) = |d_f(t)|^2$

- A key role is clearly played by the matrix element $\kappa(t) = \langle\, \phi_f^{(0)}\,|\hat{H}'(t')|\,\phi_i^{(0)}\,\rangle$ of the perturbation between the initial and final states. We had already alluded to this a few times earlier.
- The second main contribution is an oscillating factor depending on the energy difference $\Delta E = E_f^{(0)} - E_i^{(0)}$ between the initial and final states. This can interplay with any time-dependence in $\kappa(t)$ and will be responsible for resonance features as we shall see shortly.
- We will stop at first order here, but see a more systematic approach for generalisation to higher orders in section 9.4.

Example 70, Kicked harmonic oscillator: (also see Shankar page 476). Consider a harmonic oscillator (section 2.3), which is in its ground-state $|\,\phi_0\,\rangle$ at $t = -\infty$ and then subject to a time-dependent perturbation

$$\hat{H}'(t) = -F\hat{x}e^{-t^2/\tau^2}. \tag{9.11}$$

We had seen the perturbation without time-dependence in example 55, and hence know that (9.11) describes the application of a short kick by a homogeneous force near time $t = 0$ of duration $\sim \tau$. What is the probability that this kick has excited the oscillator into state $|\,\phi_n\,\rangle$ by time $t = \infty$?

Example continued: To first order perturbation theory, we know from Eq. (9.10) that for $n > 0$

$$d_n(\infty) = +\frac{i}{\hbar}F\int_{-\infty}^{\infty} dt' \;\; e^{in\omega t'}\langle\, \phi_n \,|\hat{x}|\, \phi_0 \,\rangle e^{-t'^2/\tau^2}. \tag{9.12}$$

We can evaluate $\langle\, \phi_n \,|\hat{x}|\, \phi_0 \,\rangle = \sqrt{\hbar/(2m\omega)}$ using $\hat{x} = (\hat{a} + \hat{a}^\dagger)\sqrt{\hbar/(2m\omega)}$, thus at most excitation into state $n = 1$ in possible to this order of perturbation theory. The remaining integral over time t' can be solved by mathematica or with techniques as in section 2.6 and we reach a transition probability

$$P = |d_1(\infty)|^2 = +\frac{F^2\pi\tau^2}{2m\omega\hbar}e^{-\omega^2\tau^2/4}. \tag{9.13}$$

This has lots of reasonable properties: It increases for stronger or longer kicks, and reduces for higher oscillator frequencies (larger energy difference between states 0 and 1). We will revisit the result shortly.

Eq. (9.10) works for any time-dependence of the perturbation, but we might not be able to find a nice closed form solution for all time-dependences. Now let's look at three extreme cases for the time-dependence of the perturbation, in the following three subsections. For all of these we later also go beyond perturbation theory, in section 9.2 and section 9.3.

9.1.2 Sudden perturbation

Consider a finite perturbation, starting at $t = 0$ (hence $\hat{H}'(t) = 0$ for $t < 0$) and changing the Hamiltonian to $\hat{H}_f$ within some very short (infinitesimal) time t_ϵ. It is clear that at the early time t_ϵ the transition probability to any other state than i vanishes, since

$$\lim_{t_\epsilon\to 0} d_f(t_\epsilon) = \lim_{t_\epsilon\to 0} -\frac{i}{\hbar}\int_0^{t_\epsilon} dt' \;\; e^{i(E_f^{(0)}-E_i^{(0)})t'/\hbar}\langle\, \phi_f^{(0)} \,|\hat{H}'(t')|\, \phi_i^{(0)} \,\rangle = 0. \tag{9.14}$$

Thus immediately after the transition, the state has remained the same as before. The quantum system "needs some time to respond to the perturbation". We will see in section 9.2.1 that this is true also beyond perturbation theory.

Similarly, if we look at example 70 and consider the limit $\tau \to 0$ of a very short, sudden kick given the harmonic oscillator, the transition probability Eq. (9.13) vanishes.

9.1.3 Adiabatic perturbation

Now let's look at the opposite limit, namely a very slow change of the Hamiltonian. We will illustrate this with the

Example 71, Adiabatic change of a two-level system: Consider any two-level system, that we can thus consider as a pseudo spin-1/2 (see section 4.7.4), with Hamiltonian:

$$\hat{H} = \underbrace{\Delta|\uparrow\rangle\langle\uparrow|}_{=\hat{H}^{(0)}} + \underbrace{\kappa(t)\big(|\uparrow\rangle\langle\downarrow| + |\downarrow\rangle\langle\uparrow|\big)}_{=\hat{H}'(t)} \tag{9.15}$$

or in matrix form

$$\underline{\underline{H}} = \begin{pmatrix} 0 & \kappa(t) \\ \kappa(t) & \Delta \end{pmatrix}. \tag{9.16}$$

where the coupling between the two states changes linearly from zero to a final value κ_0 over the time interval T:

$$\kappa(t) = \begin{cases} 0 & \text{for } t < 0, \\ \kappa_0 \frac{t}{T} & \text{for } 0 < t < T, \\ \kappa_0 & \text{for } T < t. \end{cases} \tag{9.17}$$

Suppose we start in $|\downarrow\rangle$. According to (9.10) the transition amplitude into $|\uparrow\rangle$ is $d_\uparrow(t) = -\frac{i}{\hbar}\int_0^t dt' \; e^{i\Delta t'/\hbar}\kappa(t)$ and hence

$$d_\uparrow(T) = -\frac{i}{\hbar}\int_0^T dt' \; e^{i\Delta t'/\hbar}\frac{t}{T} = \frac{i\hbar\kappa(1-e^{i\Delta T/\hbar}) - \kappa\Delta T e^{i\Delta T/\hbar}}{\Delta^2 T} \overset{T\to\infty}{\to} -\frac{\kappa}{\Delta}e^{i\Delta T/\hbar} \tag{9.18}$$

Now we can also find the perturbed eigenstate of the Hamiltonian at $t > T$ using time-independent perturbation theory with Eq. (7.21) and find

$$|\phi_1\rangle = |\downarrow\rangle - \frac{\kappa}{\Delta}|\uparrow\rangle \tag{9.19}$$

We have thus seen in the context of perturbation theory, that for a very slow (we say adiabatic) change of the Hamiltonian, a quantum state in an eigenstate of the Hamiltonian before the change, ends up in the corresponding eigenstate after the change (up to a phase factor).

Again we will see in section 9.2.2 that this result is also true beyond perturbation theory.

9.1.4 Periodic perturbation

Finally, let us assume the perturbation is sinusoidal

$$\hat{H}'(t) = \hat{V}\cos(\omega t), \tag{9.20}$$

with $\hat{V}$ an arbitrary "small" but time-independent operator. Application of (9.10) with $f \neq i$ and defining the transition frequency $\omega_{fi} = (E_f^{(0)} - E_i^{(0)})/\hbar$ gives

$$d_f(t) = -\frac{i}{\hbar} \underbrace{\langle\, \phi_f^{(0)}\, |\hat{V}|\, \phi_i^{(0)}\, \rangle}_{\equiv V_{fi}} \int_0^t dt'\ e^{i\omega_{fi}t'} \cos(\omega t') = -\frac{iV_{fi}}{2\hbar} \int_0^t dt'\ \left[e^{i(\omega_{fi}+\omega)t'} + e^{i(\omega_{fi}-\omega)t'}\right]$$

$$= -\frac{V_{fi}}{2\hbar} \left[\frac{e^{i(\omega_{fi}+\omega)t} - 1}{\omega_{fi}+\omega} + \frac{e^{i(\omega_{fi}-\omega)t} - 1}{\omega_{fi}-\omega} \right]. \tag{9.21}$$

Let us now further assume $\omega_{fi} > 0$ and that the frequency of the perturbation is near resonant (but not exactly resonant) with the transition frequency, such that

$$\omega_{fi} + \omega \gg |\omega_{fi} - \omega|, \tag{9.22}$$

which means we can discard the first term in (9.21) due to the denominator, and reform the rest as

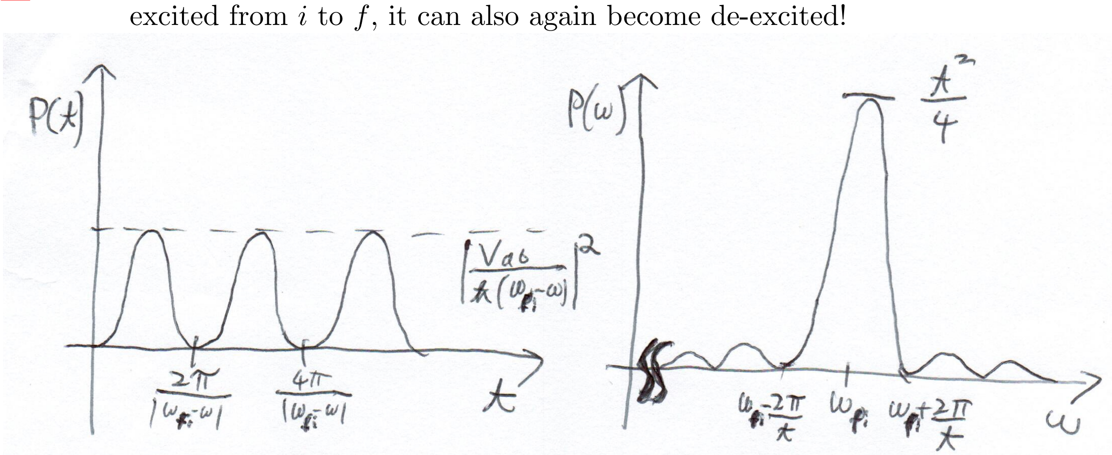
$$d_f(t) = -\frac{V_{fi}}{2\hbar} \frac{e^{i(\omega_{fi}-\omega)t/2}}{\omega_{fi}-\omega} \left[e^{i(\omega_{fi}-\omega)t/2} - e^{-i(\omega_{fi}-\omega)t/2} \right] = -i\frac{V_{fi}}{\hbar} \frac{e^{i(\omega_{fi}-\omega)t/2}}{\omega_{fi}-\omega} \sin\left[(\omega_{fi}-\omega)t/2\right]. \tag{9.23}$$

Finally taking the mod square $P_f(t) = |d_f(t)|^2$, we have the

Transition probability from a periodic perturbation to first order time-dependent perturbation theory as:

$$P_f(t) = \frac{|V_{fi}|^2}{\hbar^2 |\omega_{fi} - \omega|^2} \sin^2\left[(\omega_{fi} - \omega)\frac{t}{2}\right]. \tag{9.24}$$

- The transition probability remains a function of time and in fact oscillates between a small [21] value $P_{\max} = |V_{fi}|^2/(\hbar^2|\omega_{fi} - \omega|^2)$ and zero. Thus while initially the system might be excited from i to f, it can also again become de-excited!



top: Transition probability (9.24) as a function of time (left) and perturbation frequency (right)

[21] If it was not small, we would not have been justified to use perturbation theory.

- The period of these oscillations in the excitation probability is controlled by the detuning $\Delta = \omega_{fi} - \omega$ of the perturbation from the resonance frequency.
- The closer we are to resonance (the smaller Δ), the larger the maximum probability to make the transition from i to f. However we have to be careful here, that once $P_{\max}$ becomes too large, perturbation theory ceases to be valid. We shall see the corresponding non-perturbative result in section 9.3.5 and show that even $P_f(t) = 1$ can be reached.
- We can also look at the dependence of $P_f(t)$ on ω at fixed t, which is also drawn above. This function is called a "sinc function" $(\sin(x)/x)$. We can see by the indicated width and height of the main peak, that it converges against a delta-function as $t \to 0$.

For an example please be patient for section 9.3, which is an entire "example section" for this result.

9.2 Extreme time dependences beyond perturbation theory

The applications of perturbation theory in the subsections of section 9.1 contained quite extreme time-dependences (extremely fast, extremely slow, and perfectly periodic). It turns out the first two are nices cases that we can also understand going completely beyond perturbation theory, i.e. considering the complete time dependence due to the TDSE (3.8) without any need for small changes.

9.2.1 Sudden quench of the Hamiltonian

Let us assume the Hamiltonian changes very suddenly, at time $t = 0$, within a very short time interval τ_ϵ from $\hat{H}(t = 0) = \hat{H}^{(i)}$ to $\hat{H}(t = \tau_\epsilon) = \hat{H}^{(f)}$. This is also referred to as a quench of the Hamiltonian. Our discussion in section 9.1.2 was a special case of this, where the change from $\hat{H}^{(i)}$ to $\hat{H}^{(f)}$ was not only fast but also "small". In this section, we will drop the requirement for it to be small, but the change should remain finite.

Suppose the quantum system was in some arbitrary state $|\,\Psi_0\,\rangle$ initially. Here we can tell without perturbation theory, what will be the state immediately after the change, at τ_ϵ. Revisit section 3.9 on time evolution. Instead of (3.58), since the Hamiltonian is time-dependent, we have to write:

$$|\,\Psi(t)\,\rangle = e^{-i\int_0^t \frac{\hat{H}(t')}{\hbar}dt'}|\,\Psi(0)\,\rangle = \hat{U}(t,0)|\,\Psi(0)\,\rangle. \tag{9.25}$$

Using this, we know that

$$|\,\Psi(\tau_\epsilon)\,\rangle = e^{-i\int_0^{\tau_\epsilon} \frac{\hat{H}(t')}{\hbar}dt'}|\,\Psi(0)\,\rangle, \tag{9.26}$$

For an infinitesimal τ_ϵ the integral vanishes since the integrand is finite, and $|\,\Psi(\tau_\epsilon)\,\rangle = |\,\Psi_0\,\rangle$. This is nothing new, also in classical mechanics no physical system would respond to a perturbation instantaneously, but always responds delayed with some inertia.

Of course, in reality, a Hamiltonian will never change instantaneously. The sudden approximation will be appropriate if the change happens within a duration τ such that $\tau \ll \frac{2\pi}{\omega_n - \omega_m}$, with $\omega_n = E_n/\hbar$ the natural frequencies of the initial Hamiltonian.