Notes for Lecture 13

Time-dependent perturbation

We now discuss the time-*dependent* perturbation theory. This will shed light on the missing physics so far. The question is the following. If a quantum mechanical system has certain energy levels, how does one probe them? The answer is "using external probes." More specifically, a spectroscopic probe uses a time-dependent perturbation that induces the excitation or the de-excitation, which is an essential process by which we get to know quantum energy levels or on which important physical processes such as the light amplification in laser are built.

13.1 Perturbation treatment

Eq. 12.13 is exact within the two level model, and is ready for our perturbation treatment, since only the right hand side is proportional to the perturbing Hamiltonian $\hat{H}_1$.

$$\left.\begin{aligned} \dot{C}_0(t) &= \frac{C_0(t)}{i\hbar}\,{}_0\langle \hat{H}_1(t)\rangle_0 + \frac{C_1(t)e^{-i\omega_{1,0}t}}{i\hbar}\,{}_0\langle \hat{H}_1(t)\rangle_1 \\ \dot{C}_1(t) &= \frac{C_0(t)e^{i\omega_{1,0}t}}{i\hbar}\,{}_1\langle \hat{H}_1(t)\rangle_0 + \frac{C_1(t)}{i\hbar}\,{}_1\langle \hat{H}_1(t)\rangle_1 \end{aligned}\right\} \tag{12.13}$$

General comment

Eq. 12.13 is a particularly nice equation to solve perturbatively. We identify the unknown variables as $C_0(t)$ and $C_1(t)$. Then, Eq. 12.13 can be rewritten simply as

$$L = R \tag{13.1}$$

where

$$L \equiv \begin{pmatrix} \dot{C}_0(t) \\ \dot{C}_1(t) \end{pmatrix} = \frac{d}{dt} \begin{pmatrix} C_0(t) \\ C_1(t) \end{pmatrix} \tag{13.2}$$

and

$$R \equiv \frac{1}{i\hbar} \begin{pmatrix} {}_0\langle \hat{H}_1(t) \rangle_0 & e^{-i\omega_{1,0}t}\,{}_0\langle \hat{H}_1(t) \rangle_1 \\ e^{i\omega_{1,0}t}\,{}_1\langle \hat{H}_1(t) \rangle_0 & {}_1\langle \hat{H}_1(t) \rangle_1 \end{pmatrix} \begin{pmatrix} C_0(t) \\ C_1(t) \end{pmatrix} \tag{13.3}$$

This form of equation

$$L = R \qquad \text{with } R \propto \hat{H}_1 \propto \delta \equiv \text{ a small perturbation parameter}$$

is precisely the form that admits a perturbation solution (page 4 of LN 3). What is more in the current case is that *both* L and R are *linear* functions of the unknowns ($C_0(t)$ and $C_1(t)$). What is so good about this linearity? The perturbative solution can be viewed as almost error-free due to it. The reason is the following. Suppose that we have a perturbation solution correct up to order δ^j in our hand. We plug in that solution to R, and we get an approximation R_{j+1}. Since $R \propto \delta$ and R is linear in $C_0(t)$ and $C_1(t)$, we see that R_{j+1} contains terms up to order δ^{j+1} and *precisely* up to that order, and no more higher order terms! Besides, since L is also linear, when we solve the perturbation equation $L = R_{j+1}$, we get solutions for $C_0(t)$ and $C_1(t)$, which contain terms up to order δ^{j+1}, and *precisely* up to that order, and no more higher order terms! Such a solution is precisely what we are entitled to obtain in the $(j+1)$-th order loop of the perturbation theory (page 4 of LN 3), as any higher order terms are not correct. Due to the linearity of L and R, any incorrect terms *automatically never* appear, making the perturbation process worry free! Compare this situation with a general case when non-linearity is involved (e.g., page 4 of LN 10), in which case more care must be exercised.

More precisely stated, we just established the following for this *very* problem, where both L and R are *linear* in C_n. If we plug in the j-th order *correction* $C_n^{(j)}$ to R, then that gives the $(j+1)$-th order correction term for R_{j+1}, which we can denote as $R_{j+1}^{(j+1)}$. If we then solve for the *particular solution* (that vanishes at $t = 0$) of the first order differential equation, $L = R_{j+1}^{(j+1)}$, then that solution corresponds precisely to $C_n^{(j+1)}$.

Having established this very nice fact for this problem at hand, please do also note that it is extremely easy to obtain the solution up to the first order, even without knowing this fact clearly. For the most part, all we need for certain narrow purposes of this course will be the solutions up to the first order.

Zeroth order solution

If we ignore the right hand side completely, then we get the zeroth order equation to solve

$$\dot{C}_0(t) \;=\; \dot{C}_1(t) \;=\; 0 \tag{13.4}$$

So, at the zeroth order, both $C_0(t)$ and $C_1(t)$ are independent of time. This is what we already anticipated in the previous section. In particular, let us assume that initially the system is in the state $|0\rangle$, then we get

$$\left.\begin{aligned} C_0^{(0)}(t) &= 1 \\ C_1^{(0)}(t) &= 0 \end{aligned}\right\} \qquad \text{zeroth order solution} \tag{13.5}$$

First order correction

We plug in the zeroth order solution to the right hand side of Eq. 12.13 and get the first order equation to solve.

$$\left.\begin{aligned} \dot{C}_0(t) &= \frac{{}_0\big\langle \hat{H}_1(t)\big\rangle_0}{i\hbar} \\ \dot{C}_1(t) &= \frac{e^{i\omega_{1,0}t}\;{}_1\big\langle \hat{H}_1(t)\big\rangle_0}{i\hbar} \end{aligned}\right\} \tag{13.6}$$

Solving this set of equations, we get $C_0(t) = 1 + \int_0^t dt' \, \frac{{}_0\langle \hat{H}_1(t')\rangle_0}{i\hbar}$. Notice, as explained above, this solution is very neat, since it does not contain any spurious second order or higher terms, which would have to be thrown away at this point. The second term (which corresponds to a particular solution of the differential equation) is the first order correction, $C_0^{(1)}(t)$. For $C_1(t)$, we get, by integrating the above equation, $C_1(t) = \int_0^t dt' \, e^{i\omega_{1,0}t'} \, \frac{{}_1\langle \hat{H}_1(t')\rangle_0}{i\hbar}$, which is identified as $C_1^{(1)}(t)$. Both solutions can be summarized as

$$C_n^{(1)}(t) \;=\; \int_0^t dt' \left(\frac{e^{i\omega_{n,0}t'}}{i\hbar}\right) {}_n\big\langle \hat{H}_1(t')\big\rangle_0 \qquad \text{first order correction} \tag{13.7}$$

where $n = 0, 1$ (and $\omega_{0,0} = \omega_0 - \omega_0 = 0$). In this solution, we have assumed that $t = 0$ is the initial time. However, this convention can be changed since time is homogeneous. For instance, $t = -\infty$ as the initial time is another useful choice in some context.

Second order correction

Exploiting the *linearity* of the perturbation equation, as discussed above, in order to get the second order correction, all we need to do is to plug in the first order correction to the right hand side of Eq. 12.13, and then integrating it to get the particular solution. Thus, we get

$$\begin{aligned}
C_0^{(2)}(t) &= \int_0^t dt' \left[\frac{C_0^{(1)}(t')}{i\hbar} \, {}_0\big\langle \hat{H}_1(t') \big\rangle_0 + \frac{C_1^{(1)}(t') e^{-i\omega_{1,0}t'}}{i\hbar} \, {}_0\big\langle \hat{H}_1(t') \big\rangle_1 \right] \\
C_1^{(2)}(t) &= \int_0^t dt' \left[\frac{C_0^{(1)}(t') e^{i\omega_{1,0}t'}}{i\hbar} \, {}_1\big\langle \hat{H}_1(t') \big\rangle_0 + \frac{C_1^{(1)}(t')}{i\hbar} \, {}_1\big\langle \hat{H}_1(t') \big\rangle_1 \right]
\end{aligned}$$

Note that this equation can be re-written as, using, $\omega_{n,n} = 0$ and $\omega_{m,n} = -\omega_{n,m}$,

$$C_n^{(2)}(t) = \sum_m \int_0^t dt' \left(\frac{e^{i\omega_{n,m}t'}}{i\hbar} \right) {}_n\big\langle \hat{H}_1(t') \big\rangle_m C_m^{(1)}(t') \tag{13.8}$$

where $m = 0, 1$, as is n. Plugging in Eq. 13.7 (with the dummy variable change $t' \to t''$) into the right hand side, we get **the second order correction**:

$$C_n^{(2)}(t) = \sum_m \int_0^t dt' \left(\frac{e^{i\omega_{n,m}t'}}{i\hbar} \right) {}_n\big\langle \hat{H}_1(t') \big\rangle_m \int_0^{t'} dt'' \left(\frac{e^{i\omega_{m,0}t''}}{i\hbar} \right) {}_m\big\langle \hat{H}_1(t'') \big\rangle_0 \tag{13.9}$$

[*Advanced topic; recommended for everyone's reading!*] Reading this solution from right to left is of essential help to see what this perturbation theory is all about. First, there is state 0. Then, at time t'', the state changes ("scatters") to m. Then, at time t', there is a change of state ("scattering") from m to n. The exponential factors $e^{i\omega_{n,m}t'} \cdot e^{i\omega_{m,0}t''}$ can be seen as the phase factor accumulated due to the time evolution, by $\hat{H}_0$ alone, at different intervals divided by scattering events. Each "scattering" event in this description is the so-called "vertex" in the language Feynman diagram. ${}_n\big\langle \hat{H}_1(t') \big\rangle_m / (i\hbar)$ is the quantity associated with each vertex.

Correction to any order

Clearly, Eq. 13.8 can be re-written as

$$C_n^{(j+1)}(t) = \sum_m \int_0^t dt' \left(\frac{e^{i\omega_{n,m}t'}}{i\hbar} \right) {}_n\big\langle \hat{H}_1(t') \big\rangle_m C_m^{(j)}(t') \qquad j = 0, 1, 2, \ldots \tag{13.10}$$

Using this recursion relation, it can be seen $C_n^{(j)}$ will involve j-fold integral in time (double integral for the second order correction as seen in Eq. 13.9, triple integral in time for the third order correction, etc.). While it is seen how the expression for higher order correction will be increasingly complicated, it is also obvious that it will follow the pattern as described in the "*advanced topic*" discussion above with the number of vertices to consider as dictated by the order of the perturbation.

Notation

The textbook uses the superscript $^{(n)}$ to mean the solution that includes terms *from* the zeroth order term through the n-th order term. Note that this convention is different from the convention used throughout the lecture notes, which follow the more conventional notation where $^{(n)}$ means *the n-th order term only*.

Which order solution do we need?

For most things that we are interested in this course, the first order correction, Eq. 13.7 is singularly important. That solution is pretty much all we need for all practical purposes of this course.

It is important to note the following points.

1. There is no first order correction to $|C_n|^2$.
2. The second order correction to $|C_n|^2$ is determined completely by $C_n^{(1)}$.
3. The probability sum rule, $\sum_n |C_n|^2 = 1$ is satisfied exactly for the perturbation solution up to j-th order for any j: $C_n(t) \approx C_n^{(0)} + C_n^{(1)}(t) + ... + C_n^{(j)}(t)$.

All of these important points will be clarified by your work (homework). Point 2 is of great importance, as we point out next.

Transition probability

This is the main quantity of our interest. In the context of our current two level problem, we ask, "what is the transition probability that state 0 will transition to state 1?". The answer is $|C_1(t)|^2$, as that gives the probability for state 1 to be occupied at time t. Since $C_1^{(0)} = 0$ by assumption, the first order correction, Eq. 13.7, is all there is for $C_1(t)$. Thus, we get

$$P_{0\to 1}(t) \;=\; |C_1(t)|^2 \;\approx\; \left| \int_0^t dt' \left(\frac{e^{i\omega_{1,0}t'}}{i\hbar} \right) {}_1\!\left\langle \hat{H}_1(t') \right\rangle_0 \right|^2 \tag{13.11}$$

By point 2 above, this expression is correct up to *second* order. In fact, this **transition probability** is *of second order* in perturbation.

13.2 Sinusoidal perturbation

Let us consider a sinusoidal perturbation[1]

$$\hat{H}_1(t) \;=\; \hat{V}^\dagger \exp(i\omega t) + \hat{V} \exp(-i\omega t) \tag{13.12}$$

where any dependence on $\hat{\vec{r}}$ or $\hat{\vec{p}}$ (or any other dynamical variable such as spin or orbital angular momentum) of $\hat{H}_1$ is implicit in $\hat{V}$, which is however not explicitly dependent on time. Note that $\hat{H}_1$, as defined in terms of $\hat{V}$ and its Hermitian conjugate $\hat{V}^\dagger$, is Hermitian. Note also that $\hat{V}$ by itself is *not* Hermitian, in general. We get

$${}_1\!\left\langle \hat{H}_1(t) \right\rangle_0 \;=\; V_{1,0} \exp(-i\omega t) + V_{0,1}^* \exp(i\omega t) \tag{13.13}$$

where use has been made of the fact that

$$\left\langle 1 \left| \hat{V}^\dagger \right| 0 \right\rangle \;=\; \left\langle 0 \left| \hat{V} \right| 1 \right\rangle^* \;=\; V_{0,1}^* \tag{13.14}$$

and similarly for a general matrix element $V_{m,n}$. The first order solution for $C_1(t)$ is given solely by Eq. 13.7,

$$\begin{aligned} C_1(t) \;&\approx\; \frac{1}{i\hbar} \int_0^t dt' \left(V_{0,1}^*\, e^{i(\omega_{1,0}+\omega)t'} + V_{1,0}\, e^{i(\omega_{1,0}-\omega)t'} \right) \\ &=\; -\frac{1}{\hbar} \left[V_{0,1}^* \frac{e^{i(\omega_{1,0}+\omega)t} - 1}{\omega_{1,0}+\omega} + V_{1,0} \frac{e^{i(\omega_{1,0}-\omega)t} - 1}{\omega_{1,0}-\omega} \right] \end{aligned} \tag{13.15}$$

Let us assume a typical case (a **near resonance** case) where $\omega \approx \omega_{1,0}$, while $\omega_{1,0} > 0$. This assumption can be viewed as a natural one to make in a problem that can be

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[1] Here, we are *not* assuming that $H_1 = V\cos(\omega t)$ (cf. textbook). The reason why we do not do it is because in the current problem "$\exp(\pm i\omega t)$" is *really much more* physical than "$\cos(\omega t)$" or "$\sin(\omega t)$." If we express our perturbation as a single real function, then we can write $H_1 = 2|V|\cos(\omega t + \phi)$, where $V = |V|\exp(i\phi)$. In classical mechanics, the complex plane can be viewed as a mere mathematical convenience. In quantum mechanics, it is essential. In the current case, we shall see that the two terms, the $\exp(i\omega t)$ term and the $\exp(-i\omega t)$ term, describe different physics, emission and absorption respectively.

approximated well with a two level model. Why? Otherwise, we will have a hard time justifying why we picked out only these two levels among many energy levels of the system. Only near resonance, the response of two energy levels is singularly more important than any other pair of energy levels, whose energy difference is quite different from the frequency of the perturbation. Also, it is clear that $C_1(t)$ will be much smaller if $\omega \gg \omega_{1,0}$ or $\omega \ll \omega_{1,0}$ (keep in mind that $\omega \geq 0$ by definition), than compared to what it will be if $\omega \approx \omega_{1,0}$. Clearly, near resonance, the second term is dominant, and we get

$$\begin{aligned} C_1(t) &\approx -\frac{V_{1,0}}{\hbar}\left[\frac{e^{i(\omega_{1,0}-\omega)t}-1}{\omega_{1,0}-\omega}\right] \\ &= -\frac{V_{1,0}}{\hbar}\, e^{\frac{i(\omega_{1,0}-\omega)t}{2}}\left[\frac{e^{\frac{i(\omega_{1,0}-\omega)t}{2}}-e^{\frac{-i(\omega_{1,0}-\omega)t}{2}}}{\omega_{1,0}-\omega}\right] \\ &= -i\,\frac{2V_{1,0}}{\hbar}\cdot e^{\frac{i(\omega_{1,0}-\omega)t}{2}}\cdot\frac{\sin\frac{(\omega-\omega_{1,0})t}{2}}{\omega-\omega_{1,0}} \end{aligned} \tag{13.16}$$

which means that the **transition probability** is given by

$$P_{0\to 1}(t) = |C_1(t)|^2 \approx \frac{4|V_{1,0}|^2}{\hbar^2}\cdot\frac{\sin^2\frac{(\omega-\omega_{1,0})t}{2}}{(\omega-\omega_{1,0})^2} \tag{13.17}$$

This probability oscillates. Noting that $\sin^2\frac{\theta}{2} = \frac{1-\cos\theta}{2}$, we see that the probability oscillates at angular frequency given by $|\omega-\omega_0|$. Why at this frequency? The fact that such an oscillation exists is a consequence of the interference in the time domain. You may consider this an analogous phenomenon to an interference pattern generated in space by a single slit. Eq. 13.7 is the integral of all amplitudes of the quantum mechanical probability wave as it propagates from time 0 to time t. As we saw above, this integral is proportional to the integral $\int_0^t dt' \exp\left(i(\omega_{1,0}-\omega)t'\right)$ near resonance. This factor is simply the sum over all phase factors for all different paths that correspond to all possibilities in which the initial wave, the state $|0\rangle$, will scatter once (since we are dealing with the first order perturbation effect only) at some time t' to turn into the final wave, the state $|1\rangle$. In analogy with a single (Young's) slit problem, in the current case, we have a completely destructive interference if t is such that $(\omega_N-\omega)t = 2m\pi$ (recall $\omega_N = \omega_{1,0}$ from Eq. 12.4) for any non-zero integer m, which explains why angular frequency of the oscillation is given by $|\omega-\omega_0|$, and there is a zero transition probability for these t values (including $m = 0$ giving $t = 0$, which corresponds to $P_{0\to 1} = 0$ due to the initial condition).

$$P_{0\to 1}(t) = 0 \qquad\qquad \text{if } t = \frac{2\pi}{|\omega_N-\omega|}\cdot m \text{ with } m = 0, 1, 2, ... \tag{13.18}$$

Of course, the reason why we consider $t \geq 0$ is because we consider the initial time be[2] 0. For the same reason, the probability vanishes as a function of ω, if for a given

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[2] So, the perturbation can be considered to be "turned on" at $t = 0$, while non-existent at $t < 0$.

value of t,

$$P_{0\to1}(t) \;=\; 0 \qquad\qquad \text{if } \omega = \omega_N \pm \frac{2\pi}{t} m \text{ with } m = 1, 2, \ldots. \tag{13.19}$$

In this expression, $m = 0$ must be excluded since it corresponds to the on-resonance condition $\omega = \omega_{1,0} = \omega_N$. Note that on-resonance, or very close to it, $\sin\left(\frac{(\omega-\omega_N)t}{2}\right) \approx \frac{(\omega-\omega_N)t}{2}$ as long as $t \ll \frac{2\pi}{|\omega-\omega_N|}$, and we get

$$P_{0\to1}(t) \;\approx\; \frac{|V_{1,0}|^2\, t^2}{\hbar^2} \qquad\qquad 0 \le t \ll \frac{2\pi}{|\omega-\omega_N|} \tag{13.20}$$

This expression may look as if it suggests that the probability is increasing indefinitely as a quadratic function of t if we are sufficiently close to the resonance condition. However, it *must* be kept in mind that the (dimensionless) perturbation parameter ("δ") itself is given by

$$\delta \;\equiv\; \frac{|V_{1,0}|t}{\hbar} \tag{13.21}$$

up to a numerical factor, and so our theory breaks down if $P_{0\to1}(t)$ becomes a significant fraction of 1. In such a case, higher order perturbation terms must be summed over, if possible, to give $P_{0\to1}(t)$. Better still would be an exact solution, if available, which formally corresponds to the summation over perturbation terms of all orders. Such an example will be examined in a homework problem. As expected on physical grounds, $P_{0\to1}$ never exceeds 1 in such a solution.

Examine Figures T9.1 and T9.2 with these points in mind.

13.3 Any initial state, multiple states

Now, we consider generalization from a simple two level model. The good news is that the derivation above was left as very general already. The work that we must do to generalize our result to make it applicable to any complicated physical situation is not much.

Any initial state

What is the initial state is given by $|1\rangle$, not $|0\rangle$? Then, all we need to do is to change 0 to 1 in Eq. 13.7. Let us say that the initial state is $i = 0$ or 1 or any other state index (see below). That is, let us assume that our initial state is a more general one

$$C_n^{(0)} \;=\; \delta_{n,i} \tag{13.22}$$

Then, Eq. 13.7 changes to[3]

$$C_n^{(1)}(t) = \int_0^t dt' \left(\frac{e^{i\omega_{n,i}t'}}{i\hbar} \right) {}_n\big\langle \hat{H}_1(t') \big\rangle_i \qquad \text{first order correction} \qquad (13.23)$$

Therefore, if $i = 1$ instead of 0, then instead of Eq. 13.15 we will be interested in C_0, which is obtained simply by swapping indices 0, 1 in Eq. 13.15

$$C_0(t) \approx -\frac{1}{\hbar}\left[V_{1,0}^* \frac{e^{i(\omega_{0,1}+\omega)t} - 1}{\omega_{0,1} + \omega} + V_{0,1} \frac{e^{i(\omega_{0,1}-\omega)t} - 1}{\omega_{0,1} - \omega} \right] \qquad (13.24)$$

Now that $\omega_{0,1} < 0$ by assumption, we see that the first term, rather than the second term, contains the resonance effect. Therefore, near resonance, we have

$$\begin{aligned} C_0(t) &\approx -i\,\frac{2V_{1,0}^*}{\hbar} \cdot e^{\frac{i(\omega_{0,1}+\omega)t}{2}} \cdot \frac{\sin\frac{(\omega+\omega_{0,1})t}{2}}{\omega + \omega_{0,1}} \\ &= -i\,\frac{2V_{1,0}^*}{\hbar} \cdot e^{\frac{i(\omega-\omega_{1,0})t}{2}} \cdot \frac{\sin\frac{(\omega-\omega_{1,0})t}{2}}{\omega - \omega_{1,0}} \qquad \because\ \omega_{0,1} = -\omega_{1,0} \qquad (13.25) \end{aligned}$$

Thus, the transition probability is given by

$$P_{1\to 0}(t) = |C_0(t)|^2 \approx \frac{4|V_{1,0}|^2}{\hbar^2} \cdot \frac{\sin^2\frac{(\omega-\omega_{1,0})t}{2}}{(\omega - \omega_{1,0})^2} \qquad (13.26)$$

Note that this probability is the same as Eq. 13.17. Quite generally this probability represents an **emission probability** while Eq. 13.17 represents an **absorption probability**. That the two transition probabilities are exactly the same is often referred to as **the principle of detailed balance**, which is a statement about the time-reversal invariance.

Now, some of you may be asking – what if the initial state is a superposition of different $\hat{H}_0$ eigenstates? This could happen. In such a case, $C_n^{(1)}$ will not consist of a single term, but will be a sum of many terms, depending on how many $\hat{H}_0$ eigenstates are involved initially. Note, however, that the recursion relation, Eq. 13.10, remains perfectly valid in this case as well, for any $j = 0, 1, 2, \ldots$

A more common case would be when the initial state is a thermal ensemble of different $\hat{H}_0$ eigenstates. In such a case, each initial state can be considered as an i-th state as we did above. For the thermal ensemble, we merely need to take the Boltzmann factor into account for each $\hat{H}_0$ eigenstate. Below, we will develop a basic formalism for dealing with general multiple cases, including such a case.

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[3] Finally, I give in to use index i, which should not be confused with $i \equiv \sqrt{-1}$. I have been avoiding using index i, as best as I can so far, for such potential confusion. However, in this case, the payback seems high enough: i can be taken to mean initial as well as any one of integers $0, 1, 2, \ldots$

Multiple states

From now on, we can also let go of the restriction of a two level model. This is easy – we just allow n to be $0, 1, 2, 3, ...$, not just 0, 1. This is a trivial change, and all results above remain valid upon this change, assuming that we reinterpret indices such as m, n, i as covering all non-negative integers.

Before we go on further, let us note that the frequency scale ω_N is a very high frequency (10^{15} Hz) for an atomic energy level (~ 1 eV), giving the time scale of a femto second as the natural period of the unperturbed system. According to Eq. 13.19, the width of the resonance peak as a function of ω is $\sim \frac{2\pi}{t}$. So, for any reasonable time scale t of an instrument, t can be considered infinite, and we see that the width of the function $P_{i\to f}(\omega)$ becomes very small compared to ω_N. That is, the resonance profile becomes very sharp.

Mathematically, we can use

$$\lim_{N\to\infty} \frac{1}{N} \frac{\sin^2 \frac{Nx}{2}}{\sin^2 \frac{x}{2}} = 2\pi\delta(x) \qquad \text{limit of Fejer kernel} \tag{13.27}$$

$$\lim_{N\to\infty} \frac{\sin^2 \frac{Nx}{2}}{x^2} = \frac{\pi}{2}\delta(x)\, N \tag{13.28}$$

to reduce the resonance absorption/emission probability formula, Eq. 13.17 or 13.26, to (by using substitution $N \to t$, $x \to \omega - |\omega_N|$)

$$P_{i\to f} = \frac{2\pi |V_{i\leftrightarrow f}|^2}{\hbar^2} \cdot \delta(\omega - |\omega_{f,i}|)\, t \qquad \text{for } t \gg \text{natural period of the system} \tag{13.29}$$

where

$$V_{i\leftrightarrow f} \equiv \begin{cases} \langle f \,|\hat{V}\,| i\rangle & \text{for absorption } (\omega_f > \omega_i) \\ \langle f \,|\hat{V}^\dagger\,| i\rangle = \langle i \,|\hat{V}\,| f\rangle^* & \text{for emission } (\omega_f < \omega_i) \end{cases} \tag{13.30}$$

Additionally, this expression remains valid even when $\omega = 0$ (i.e. a time-independent perturbation), if the perturbing potential is re-defined as $\hat{V} + \hat{V}^\dagger \to \hat{V}$ (Homework 6.1) in that case. Now, the **transition rate** R, is given by

$$R_{i\to f} = \frac{2\pi |V_{i\leftrightarrow f}|^2}{\hbar^2} \cdot \delta(\omega - |\omega_{f,i}|) = \frac{2\pi |V_{i\leftrightarrow f}|^2}{\hbar^2} \cdot \delta(\omega - |\omega_f - \omega_i|) \tag{13.31}$$

This is the so-called **"Fermi's golden rule."** Here, it is written in a way that is applicable to both absorption and emission[4].

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[4] The emission considered here is the so-called "stimulated emission."

From this form, one can consider any possibilities for the states involved in the transition.

For instance, let us imagine that there are many final states clustered around the value corresponding to the on-resonance transition condition. Clearly the transition probability is now given by

$$\begin{aligned} P_{i\to\{f\}} &= \sum_f P_{i\to f} \\ R_{i\to\{f\}} &= \sum_f R_{i\to f} \end{aligned}$$

where i is the initial state, and $\{f\}$ is the set of all possible final states represented by the sum over f. Generally, for a distribution of energy levels, it is of great convenience to consider the **density of states** function, $\rho_f(\omega_f)$, such that $\sum_f \to \int d\omega_f \rho_f(\omega_f)$. Then, we get, using Eq. 13.31,

$$\begin{aligned} R_{i\to\{f\}} &= \int d\omega_f\, \rho_f(\omega_f) \cdot \frac{2\pi |V_{i\leftrightarrow f}|^2}{\hbar^2} \cdot \delta(\omega - |\omega_f - \omega_i|) \\ &= \frac{2\pi |V_{i\leftrightarrow f}|^2}{\hbar^2} \rho_f(\tilde{\omega}_f) \qquad |\tilde{\omega}_f - \omega_i| = \omega \end{aligned} \tag{13.32}$$

Similarly, if there is a distribution of frequencies of the perturbation (e.g., due to non-monochromatic incoherent photon beam used as perturbation), then we have

$$R_{i\to f} = \frac{2\pi |V_{i\leftrightarrow f}|^2}{\hbar^2} \rho(\tilde{\omega}) \qquad |\omega_f - \omega_i| = \tilde{\omega} \tag{13.33}$$

where $\rho(\omega)$ is the density of states associated with the distribution of ω.

Clearly, a similar expression can be written down if there is a distribution of initial states, e.g. due to a thermal ensemble. In such a case, it would be the density of states times the Boltzmann factor that need to be used.

Finally, note that any combination of these cases can occur. In such a general case, a *joint* density of states would be a necessary quantity to use.