# G25.2651: Statistical Mechanics

## Notes for Lecture 16

### I. TIME-DEPENDENT PERTURBATION THEORY

#### A. The interaction picture

Consider a quantum system described by a time-dependent Hamiltonian of the form

$$\mathrm{H}(t) = \mathrm{H}_0 + \mathrm{H}_1(t)$$

In the language of perturbation theory, $\mathrm{H}_0$ is known as the unperturbed Hamiltonian and describes a system of interest such as a molecule or a condensed-phase sample such as a pure liquid or solid or a solution. $\mathrm{H}_1(t)$ is known as the perturbation, and it often describes an external system, such as a laser field, that will be used to probe the energy levels and other properties of $\mathrm{H}_0$.

We now seek a solution to the time-dependent Schrödinger equation

$$\mathrm{H}(t)|\Psi(t)\rangle = (\mathrm{H}_0 + \mathrm{H}_1(t))\,|\Psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle \tag{1}$$

subject to an initial state vector $|\Psi(t_0)\rangle$. In order to solve the equation, we introduce a new state vector $|\Phi(t)\rangle$ related to $|\Psi(t)\rangle$ by

$$|\Psi(t)\rangle = e^{-i\mathrm{H}_0(t-t_0)}|\Phi(t)\rangle \tag{2}$$

The new state vector $|\Phi(t)\rangle$ is an equally valid representation of the state of the system. In Chapter 10, we introduced the concept of *pictures* in quantum mechanics and discussed the difference between the Schrödinger and Heisenberg pictures. Eqn. (2) represents yet another picture of quantum mechanics, namely the *interaction picture*. Like the Schrödinger and Heisenberg pictures, the interaction picture is a perfectly valid way of representing a quantum mechanical system. The interaction picture can be considered as "intermediate" between the Schröginer picture, where the state evolves in time and the operators are static, and the Heisenberg picture, where the state vector is static and the operators evolve. However, as we will see shortly, in the interaction picture, both the state vector and the operators evolve in time, however, the time-evolution is determined by the perturbation $\mathrm{H}_1(t)$. Eqn. (2) specifies how to transform between the Schrödinger and interaction picture state vectors. The transformation of operators proceeds in an analogous fashion. If A denotes an operator in the Schrödinger picture, its representation in the interaction picture is given by

$$\mathrm{A}_I(t) = e^{i\mathrm{H}_0(t-t_0)/\hbar}\mathrm{A}e^{-i\mathrm{H}_0(t-t_0)/\hbar} \tag{3}$$

which is equivalent to an equation of motion of the form

$$\frac{d\mathrm{A}_I(t)}{dt} = \frac{1}{i\hbar}[\mathrm{A}_I(t), \mathrm{H}_0] \tag{4}$$

Substitution of Eqn. (2) into the time-dependent Schrödinger equation yields

$$\begin{aligned}
(\mathrm{H}_0 + \mathrm{H}_1(t))\, e^{-i\mathrm{H}_0(t-t_0)/\hbar}|\Phi(t)\rangle &= \mathrm{H}_0 e^{-i\mathrm{H}_0(t-t_0)/\hbar}|\Phi(t)\rangle + e^{-i\mathrm{H}_0(t-t_0)/\hbar}i\hbar\frac{\partial}{\partial t}|\Phi(t)\rangle \\
\mathrm{H}_1(t)e^{-iH_0(t-t_0)/\hbar}|\Phi(t)\rangle &= e^{-iH_0(t-t_0)/\hbar}i\hbar\frac{\partial}{\partial t}|\Phi(t)\rangle \\
e^{iH_0(t-t_0)/\hbar}\mathrm{H}_1(t)e^{-iH_0(t-t_0)/\hbar}|\Phi(t)\rangle &= i\hbar\frac{\partial}{\partial t}|\Phi(t)\rangle
\end{aligned} \tag{5}$$

According to Eqn. (3), the $\exp[i\mathrm{H}_0(t-t_0)/\hbar]\mathrm{H}_1(t)\exp[-i\mathrm{H}_0(t-t_0)/\hbar]$ is the interaction-picture representation of the perturbation Hamiltonian, and we will denote this operator as $H_I(t)$. Thus, the time-evolution of the state vector in the interaction picture is given a Schrödinger equation of the form

$$H_I(t)|\Phi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\Phi(t)\rangle \tag{6}$$

The initial condition to Eqn. (6), $|\Phi(t_0)\rangle$ is, according to Eqn. (2), also $|\Psi(t_0)\rangle$. In the next section, we will develop an iterative solution to Eqn. (6), which will reveal a rich structure of the propagator for time-dependent systems.

### B. Iterative solution for the interaction-picture state vector

The solution to Eqn. (6) can be expressed in terms of a unitary propagator $U_I(t;t_0)$, the interaction-picture propagator, which evolves the initial state $|\Phi(t_0)\rangle$ according to

$$|\Phi(t)\rangle = U_I(t;t_0)|\Phi(t_0)\rangle = U_I(t;t_0)|\Psi(t_0)\rangle \tag{7}$$

Substitution of Eqn. (7) into Eqn. (6) yields an evolution equation for the propagator $U_I(t;t_0)$:

$$H_I(t)U_I(t;t_0) = i\hbar\frac{\partial}{\partial t}U_I(t;t_0) \tag{8}$$

The initial condition on Eqn. (8) is $U_I(t_0;t_0) = I$. In developing a solution to Eqn. (8), we assume that $H_I(t)$ is a small perturbation, so that the solution can take the form of a sum of powers of $H_I(t)$.

A solution of this form can be generated by recognizing that Eqn. (8) can be solved formally in terms of an integral equation:

$$\begin{aligned} U_I(t;t_0) &= U_I(t_0;t_0) - \frac{i}{\hbar}\int_{t_0}^{t} dt'\ H_I(t')U_I(t';t_0) \\ &= I - \frac{i}{\hbar}\int_{t_0}^{t} dt'\ H_I(t')U_I(t';t_0) \end{aligned} \tag{9}$$

It is straightforward to verify this form solution for $U_I(t;t_0)$. Computing the time derivative of both sides gives

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}U_I(t;t_0) &= -i\hbar\frac{i}{\hbar}\frac{\partial}{\partial t}\int_{t_0}^{t} dt'\ H_I(t')U_I(t';t_0) \\ &= H_I(t)U_I(t;t_0) \end{aligned} \tag{10}$$

Thus, Eqn. (9) is a valid expression of the solution. The implicit nature of the integral equation means that an iterative procedure based on the assumption that $H_I(t)$ is a small perturbation can be easily developed. We start with a zeroth-order solution by setting $H_I(t) = 0$ in Eqn. (9), which gives the trivial result

$$U_I^{(0)}(t;t_0) = I \tag{11}$$

This solution is now fed back into the right side of Eqn. (9) to develop a first-order solution:

$$\begin{aligned} U^{(1)}(t;t_0) &= I - \frac{i}{\hbar}\int_{t_0}^{t} dt'\ H_I(t')U_I^{(0)}(t';t_0) \\ &= I - \frac{i}{\hbar}\int_{t_0}^{t} dt'\ H_I(t') \end{aligned} \tag{12}$$

The first order solution is fed back into the right side of Eqn. (9) to develop a second-order solution:

$$\begin{aligned} U^{(2)}(t;t_0) &= I - \frac{i}{\hbar}\int_{t_0}^{t} dt'\ H_I(t')U_I^{(1)}(t';t_0) \\ &= I - \frac{i}{\hbar}\int_{t_0}^{t} dt'\ H_I(t') + \left(\frac{i}{\hbar}\right)^2\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\ H_I(t')H_I(t'') \end{aligned} \tag{13}$$

and so forth, such that the $k$th-order solution is always generated from the $(k-1)$st-order solution according to the recursion formula:

$$U^{(k)}(t;t_0) = I - \frac{i}{\hbar}\int_{t_0}^{t} dt'\ H_I(t')U_I^{(k-1)}(t';t_0) \tag{14}$$

Thus, the third-order solution is given by

$$U^{(2)}(t;t_0) = I - \frac{i}{\hbar}\int_{t_0}^{t} dt'\; H_I(t') + \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\; H_I(t')H_I(t'') - \left(\frac{i}{\hbar}\right)^3 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \int_{t_0}^{t''} dt'''\; H_I(t')H_I(t'')H_I(t''') \tag{15}$$

The exact solution is then just a sum of the solutions obtained at each order:

$$U_I(t;t_0) = \sum_{k=0}^{\infty} (-1)^k \left(\frac{i}{\hbar}\right)^k \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \cdots \int_{t_0}^{t^{(k-1)}} dt^{(k)}\; H_I(t')H_I(t'')\cdots H_I(t^{(k)}) \tag{16}$$

Having seen how to generate a solution for the propagator in the interaction picture to arbitrarily high orders in the perturbation, the time evolution of the state vector $|\Phi(t)\rangle$ in the interaction picture can be determined from

$$|\Phi(t)\rangle = U_I(t;t_0)|\Phi(t_0)\rangle \tag{17}$$

and from this expression, the time evolution of the original state vector $|\Psi(t)\rangle$ in the Schrödinger picture can be determined

$$\begin{aligned} |\Psi(t)\rangle &= e^{-iH_0(t-t_0)/\hbar}|\Phi(t)\rangle \\ &= e^{-iH_0(t-t_0)/\hbar}U_I(t;t_0)|\Phi(t_0)\rangle \\ &= e^{-iH_0(t-t_0)/\hbar}U_I(t;t_0)|\Psi(t_0)\rangle \\ &\equiv U(t;t_0)|\Psi(t_0)\rangle \end{aligned} \tag{18}$$

where we have used the fact that $|\Phi(t_0)\rangle = |\Psi(t_0)\rangle$ and, in the last line, the full propagator in the Schrödinger picture is identified as

$$U(t;t_0) = e^{-iH_0(t-t_0)/\hbar}U_I(t;t_0) \tag{19}$$

From Eqn. (19), the structure of the full propagator for the time-dependent system reveals itself. Let us use Eqn. (19) to generate the first few lowest order terms in the propagator. Substituting Eqn. (11) into Eqn. (19) yields the lowest order contribution to $U(t;t_0)$:

$$U^{(0)}(t;t_0) = e^{-iH_0(t-t_0)/\hbar} = U_0(t;t_0) \tag{20}$$

Thus, at zeroth order, Eqn. (20) implies that the system is to be propagated using the unperturbed propagator $U_0(t;t_0)$ as if the perturbation did not exist. At first order, we obtain

$$\begin{aligned} U^{(1)}(t;t_0) &= e^{-iH_0(t-t_0)/\hbar} - \frac{i}{\hbar}e^{-iH_0(t-t_0)/\hbar}\int_{t_0}^{t} dt'\; H_I(t') \\ &= e^{-iH_0(t-t_0)/\hbar} - \frac{i}{\hbar}e^{-iH_0(t-t_0)/\hbar}\int_{t_0}^{t} dt' e^{-iH_0(t'-t_0)/\hbar}\mathrm{H}_1(t')e^{-iH_0(t'-t_0)/\hbar} \\ &= e^{-iH_0(t-t_0)/\hbar} - \frac{i}{\hbar}\int_{t_0}^{t} dt'\; e^{-iH_0(t-t')/\hbar}\mathrm{H}_1(t')e^{-iH_0(t'-t_0)/\hbar} \\ &= U_0(t;t_0) - \frac{i}{\hbar}\int_{t_0}^{t} dt'\; U_0(t;t')\mathrm{H}_1(t')U_0(t';t_0) \end{aligned} \tag{21}$$

where, in the second line, the definition of $H_I(t)$ in terms of the original perturbation Hamiltonian $\mathrm{H}_1(t)$ has been used. What Eqn. (21) says is that at first order, the propagator is composed of two terms. The first term is simply the unperturbed propagation from $t_0$ to $t$. In the second term, the system undergoes unperturbed propagation from $t_0$ to $t'$ and at $t'$, the perturbation $\mathrm{H}_1(t')$ is allowed to act. From $t'$ to $t$, the system undergoes unperturbed propagation. Finally, we need to integrate over all possible intermediate times $t'$.

In a similar manner, it can be shown that up to second order, the full propagator is given by

$$U^{(2)}(t;t_0) = U_0(t;t_0) - \frac{i}{\hbar}\int_{t_0}^{t} d'\; U_0(t;t')\mathrm{H}_1(t')U_0(t';t_0) + \left(\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\; U_0(t;t')\mathrm{H}_1(t')U_0(t';t'')\mathrm{H}_1(t'')U_0(t'';t_0) \tag{22}$$

Thus, at second order, the new term involves unperturbed propagation from $t_0$ to $t''$, action of $\mathrm{H}_1(t'')$ at $t''$, unperturbed propagation from $t''$ to $t'$, action of $\mathrm{H}_1(t')$ at $t'$ and, finally, unperturbed propagation from $t'$ to $t$. Again, the intermediate times $t'$ and $t''$ must be integrated over. The picture on the left side of the equation indicates that the perturbation causes the system to undergo some undetermined dynamical process between $t_0$ and $t$. The terms on the right show how that process is broken down in terms of the action of the perturbation $\mathrm{H}_1$ at specific intermediate times. At the $k$th order, the perturbation Hamiltonian $\mathrm{H}_1$ acts on the system at $k$ specific instances in time. Because of the limits of integration, these time instances are ordered chronologically.

The specific ordering of the instances in time when $\mathrm{H}_1$ acts on the unperturbed system raises an important point. At each order the expansion for $U_I(t;t_0)$, the order in which the operators $H_I(t')$, $H_I(t'')$, etc. are multiplied is important. The reason for this is that the operator $H_I(t)$ does not commute with itself at different instances in time

$$[H_I(t), H_I(t')] \neq 0 \tag{23}$$

Thus, in order to remove any possible ambiguity when specifying the order in which operators are to be applied in a time series, we introduce the *time-ordering operator*, $T$. The purpose of $T$ is to take a product string of time-dependent operators $A(t_1)B(t_2)C(t_3)\cdots D(t_n)$ which act at different instances in time $t_1$, $t_2$,...,$t_n$ and order the operators in the product such that they act chronologically in time from the earliest time to the latest time. For example, the action of $T$ on two operators $A(t_1)$ and $B(t_2)$ is

$$T\left(A(t_1)B(t_2)\right) = \begin{cases} A(t_1)B(t_2) & t_2 < t_1 \\ B(t_2)A(t_1) & t_1 < t_2 \end{cases} \tag{24}$$

Let us now apply the time-ordering operator to the second-order term. First write the double integral as a sum of two terms generated simply interchanging the names of the dummy variables $t'$ and $t''$:

$$\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\; H_I(t')H_I(t'') = \frac{1}{2}\left[\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\; H_I(t')H_I(t'') + \int_{t_0}^{t} dt'' \int_{t_0}^{t''} dt'\; H_I(t'')H_I(t')\right] \tag{25}$$

The same region can be covered by choosing $t' \in [t_0, t]$ and $t'' \in [t', t]$. With this choice, Eqn. (25) becomes

$$\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\; H_I(t')H_I(t'') = \frac{1}{2}\left[\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\; H_I(t')H_I(t'') + \int_{t_0}^{t} dt' \int_{t'}^{t} dt''\; H_I(t'')H_I(t')\right] \tag{26}$$

In the first term on the right side of Eqn. (26), $t'' < t'$ and $H_I(t'')$ acts first, followed by $H_I(t')$. In the second term, $t' < t''$ and $H_I(t')$ acts first followed by $H_I(t'')$. The two terms can, thus, be combined with both $t'$ and $t''$ lying in the interval $[t_0, t]$ if the time-ordering operator is applied:

$$\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\; H_I(t')H_I(t'') = \frac{1}{2}\int_{t_0}^{t} dt' \int_{t_0}^{t} dt''\; T\left(H_I(t')H_I(t'')\right) \tag{27}$$

The same analysis can be applied to each order in Eqn. (16), recognizing that the number of possible time orderings of a product of $k$ operators is $k!$. Thus, Eqn. (16) can be rewritten in terms of the time-ordering operator as

$$U_I(t;t_0) = \sum_{k=0}^{\infty} (-1)^k \left(\frac{i}{\hbar}\right)^k \frac{1}{k!} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \cdots \int_{t_0}^{t} dt_k T\left(H_I(t_1)H_I(t_2)\cdots H_I(t_k)\right) \tag{28}$$

The sum in Eqn. (28) resembles the power-series expansion of an exponential, and, indeed, we can write the sum symbolically as

$$U_I(t;t_0) = T\left[\exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} dt'\; H_I(t')\right)\right] \tag{29}$$

which is known as a *time-ordered exponential*. Eqn. (29) is really a symbolic representation of Eqn. (28), in which it is understood that the time-ordering operator acts to order the operators in each term of the expansion of the exponential.

Given the formalism of time-dependent perturbation theory, we now seek to answer the following question: If the system is initially in an eigenstate of $\mathrm{H}_0$ with energy $E_i$, what is the probability as a function of time $t$ that the

system will undergo a transition to a new eigenstate of $\mathrm{H}_0$ with energy $E_f$? From the statement of the question, it is clear that the initial state vector $|\Psi(t_0)\rangle$ is simply the eigenstate of $\mathrm{H}_0$ with energy $E_i$

$$|\Psi(t_0)\rangle = |E_i\rangle \tag{30}$$

The amplitude as a function of time that the system will undergo a transition to the eigenstate $|E_f\rangle$ is obtained by propagating this initial state out to time $t$ with the propagator $U(t;t_0)$ and then taking the overlap of the resultant state with the eigenstate $|E_f\rangle$:

$$A_{fi}(t) = \langle E_f|U(t;t_0)|E_i\rangle \tag{31}$$

and the probability is just the square magnitude of this complex amplitude:

$$P_{fi}(t) = |\langle E_f|U(t;t_0)|E_i\rangle|^2 \tag{32}$$

Consider, first, the amplitude at zeroth order in perturbation theory. At this order, $U(t;t_0) = U_0(t;t_0)$, and the amplitude is simply

$$\begin{aligned} A_{fi}^{(0)}(t) &= \langle E_f|e^{-iH_0(t-t_0)/\hbar}|E_i\rangle \\ e^{-iE_i(t-t_0)/\hbar}&\langle E_f|E_i\rangle \end{aligned} \tag{33}$$

which clearly vanishes if $E_i \neq E_f$. Thus, at zeroth order, the only possibility is the trivial one in which no transition occurs.

The lowest nontrivial order is first order, where the transition amplitude is given by

$$\begin{aligned} A_{fi}^{(1)}(t) &= \langle E_f|U^{(1)}(t;t_0)|E_i\rangle \\ &= -\frac{i}{\hbar}\int_{t_0}^{t} dt'\ \langle E_f|U_0(t;t')\mathrm{H}_1(t')U_0(t';t_0)|E_i\rangle \\ &= -\frac{i}{\hbar}\int_{t_0}^{t} dt\ \langle E_f|e^{-iH_0(t-t')/\hbar}\mathrm{H}_1(t')e^{-iH_0(t'-t_0)/\hbar}|E_i\rangle \\ &= -\frac{i}{\hbar}\int_{t_0}^{t} dt'\ e^{-iE_f(t-t')/\hbar}e^{-iE_i(t'-t_0)/\hbar}\langle E_f|\mathrm{H}_1(t')|E_i\rangle \\ &= -\frac{i}{\hbar}e^{-iE_ft/\hbar}e^{iE_it_0/\hbar}\int_{t_0}^{t} dt'\ e^{i(E_f-E_i)t'/\hbar}\langle E_f|\mathrm{H}_1(t')|E_i\rangle \end{aligned} \tag{34}$$

Define a transition frequency $\omega_{fi}$ by

$$\omega_{fi} = \frac{E_f - E_i}{\hbar} \tag{35}$$

Then, taking the absolute square of the last line of Eqn. (34), we obtain the probability at first-order

$$P_{fi}^{(1)}(t) = \frac{1}{\hbar^2}\left|\int_{t_0}^{t} dt'\ e^{i\omega_{fi}t'}\langle E_f|\mathrm{H}_1(t')|E_i\rangle\right|^2 \tag{36}$$

At first order, the probability depends on the matrix element of the perturbation between the initial and final eigenstates. Thus far, the formalism we have derived is valid for any perturbation Hamiltonian $\mathrm{H}_1(t)$. If we consider the use of an external perturbation to probe the eigenvalue spectrum of $\mathrm{H}_0$, then the specific type of probe determines the form of $\mathrm{H}_1(t)$, as we saw in the first section and will explore in the next subsection.

### C. Fermi's Golden Rule

In the first section, we saw how to formulate the Hamiltonian of a material system coupled to an external electromagnetic field. Moreover, we obtained solutions for the electromagnetic field in the absence of sources or physical boundaries, namely, solutions of the free-field wave equations. In this chapter, we will focus primarily on weak fields. We will also focus on a class of experiments in which the wavelength of electromagnetic radiation is taken to be long

compared to the size of the sample under investigation. In this case, the spatial dependence of the electromagnetic field can also be neglected, since $\cos(\mathbf{k}\cdot\mathbf{r}-\omega t+\varphi_0) = \mathrm{Re}\exp(i\mathbf{k}\cdot\mathbf{r}-i\omega t+\varphi_0)$, and $\exp(i\mathbf{k}\cdot\mathbf{r}) \approx 1$ in the long-wavelength limit. In this case, it is sufficient to consider $\mathrm{H}_1(t)$ to be of the general form

$$\mathrm{H}_1(t) = -\mathcal{V}F(\omega)e^{-i\omega t} \tag{37}$$

where $\mathcal{V}$ is a Hermitian operator. (Although we could use sin and cos to express the perturbation, the form in Eqn. (37) is a particularly convenient one, and since we will be seeking probabilities of transitions, the results we obtain will be real in the end.)

Again, the question we seek to answer is given this form for the perturbation, what is the probability that the material system will be excited from an initial eigenstate $|E_i\rangle$ with energy $E_i$ to a final state $|E_f\rangle$ with energy $E_f$? However, since the perturbation is periodic in time, what we really seek to know is if the perturbation is applied over a long time interval, what is the probability per unit time or rate at which transitions will occur. Thus, in order to make the calculation somewhat easier, let us consider a time interval $T$ and choose $t_0 = -T/2$ and $t = T/2$. At first order, the transition rate $R_{fi}^{(1)}(T)$ is just the total probability $P_{fi}^{(1)}(T)$ divided by the interval length $T$:

$$R_{fi}^{(1)}(T) = \frac{P_{fi}^{(1)}(T)}{T} = \frac{1}{T\hbar^2}|F(\omega)|^2 \left| \int_{-T/2}^{T/2} e^{i(\omega_{fi}-\omega)t} dt \right|^2 |\langle E_f|\mathcal{V}|E_i\rangle|^2 \tag{38}$$

For finite $T$, the integral can be carried out explicitly yielding

$$\int_{-T/2}^{T/2} e^{i(\omega_{fi}-\omega)t} dt = \frac{\sin(\omega_{fi}-\omega)T/2}{(\omega_{fi}-\omega)/2} \tag{39}$$

Thus, the transition rate can be expressed as

$$R_{fi}^{(1)}(T) = \frac{1}{\hbar^2} T|F(\omega)|^2 |\langle E_f|\mathcal{V}|E_i\rangle|^2 \frac{\sin^2(\omega_{fi}-\omega)T/2}{[(\omega_{fi}-\omega)T/2]^2} \tag{40}$$

In the limit of $T$ very large, this expression becomes highly peaked only if $\omega_{fi} = \omega$. Otherwise, as $T \to \infty$, the expression vanishes. The condition $\omega_{fi} = \omega$ is equivalent to the condition $E_f = E_i + \hbar\omega$, which is a statement of energy conservation. Since $\hbar\omega$ is the energy quantum of the electromagnetic field, the transition can only occur if the energy of the field is exactly "tuned" for the the transition, and this "tuning" depends on the frequency of the field. In this way, the frequency of the field can be used as a probe of the allowed transitions, which then serves to probe the eigenvalue structure of $\mathrm{H}_0$.

Now, let us consider the $T \to \infty$ more carefully. We shall denote the rate in this limit simply as $R_{fi}$. In this limit, the integral becomes

$$\begin{aligned} \lim_{T\to\infty} \int_{-T/2}^{T/2} e^{-i(\omega_{fi}-\omega)t} dt &= \int_{-\infty}^{\infty} e^{i(\omega_{fi}-\omega)t} dt \\ &= 2\pi\delta(\omega_{fi}-\omega) \\ &= 2\pi\hbar\delta(E_f - E_i - \hbar\omega) \end{aligned} \tag{41}$$

Therefore, the expression for the rate in this limit can be written as

$$\begin{aligned} R_{fi}(\omega) &= \lim_{T\to\infty} \frac{P_{fi}^{(1)}(T)}{T} = \lim_{T\to\infty} \frac{1}{T\hbar^2} \left| \int_{-T/2}^{T/2} e^{i(\omega_{fi}-\omega)t} dt \right|^2 |F(\omega)|^2 \left|\langle E_f|\mathcal{V}|E_i\rangle\right|^2 \\ &= \lim_{T\to\infty} \frac{1}{T\hbar^2} \left[ \int_{-T/2}^{T/2} e^{-i(\omega_{fi}-\omega)t} dt \right] \left[ \int_{-T/2}^{T/2} e^{i(\omega_{fi}-\omega)t} dt \right] |F(\omega)|^2 \left|\langle E_f|\mathcal{V}|E_i\rangle\right|^2 \end{aligned} \tag{42}$$

where we have dropped the "(1)" superscript (it is understood that the result is derived from first-order perturbation theory), and indicate explicitly the dependence on the frequency $\omega$. When one the first integral is replaced by the $\delta$-function, the remaining integral becomes simply $T$, which cancels the $T$ in the denominator. Thus, the expression for the rate is finally

$$R_{fi}(\omega) = \frac{2\pi}{\hbar} |F(\omega)|^2 \left|\langle E_f|\mathcal{V}|E_i\rangle\right|^2 \delta(E_f - E_i - \hbar\omega) \tag{43}$$

which is known as *Fermi's Golden Rule*. It states that, to first-order in perturbation theory, the transition rate depends only the square of the matrix element of the operator $\mathcal{V}$ between initial and final states and includes, via the $\delta$-function, an energy-conservation condition. We will make use of the Fermi Golden Rule expression to analyze the application of an external monochromatic field to an ensemble of systems in order to derive expressions for the observed frequency spectra.