Fermi's Golden Rule

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Abstract

We present a proof of Fermi's Golden rule from an educational perspective without compromising formalism.

1. Introduction

Fermi's Golden Rule (also referred to as, the *Golden Rule of time-dependent perturbation theory*) is an equation for calculating transition rates. The result is obtained by applying the time-dependent perturbation theory to a system that undergoes a transition from an initial state $|i\rangle$ to a final state $|f\rangle$ that is part of a continuum of states.

The following sections provide the calculations and notions involved in deriving the final equation, as well as some concluding remarks (synopsis).

2. Time dependent perturbation theory

For a great deal of problems the time-independent perturbation theory suffices. Nevertheless, there are cases in which we want to study how systems respond to imposed perturbations and then settle into stationary states after an interval, in other words, study the transitions induced by a perturbation between stationary states of the unperturbed system. In cases like these, we use time-dependent perturbation theory to calculate, amongst other things, transition probabilities.

We assume that the hamiltonian H of the system can be written in the form:

$$H = H_0 + W(t) \tag{1}$$

where

,H_0 is the hamiltonian of the unperturbed system
,W(t) is a perturbation applied to the system.

Since H_0 is the unperturbed hamiltonian, the time independent Schrödinger equation is satisfied:

$$H_0|\varphi_n\rangle = E_n|\varphi_n\rangle \tag{2}$$

The wavefunctions $|\varphi_n\rangle$ are related to the time-dependent unperturbed wavefunctions by:

$$|\psi_n(t)\rangle = |\varphi_n\rangle e^{-iE_nt/\hbar} \tag{3}$$

The time dependent Schrödinger equation for the system is:

$$H|\psi(t)\rangle = [H_0 + W(t)]|\psi(t)\rangle = i\hbar\frac{\partial|\psi(t)\rangle}{\partial t} \tag{4}$$

with the state of the system $|\psi\rangle$, at a time t, expressed as a linear combination of the $\{|\varphi_n\rangle\}$ basis functions:

$$|\psi(t)\rangle = \sum_n c_n(t)|\psi_n(t)\rangle = \sum_n c_n(t)|\varphi_n\rangle e^{-iE_nt/\hbar} \tag{5}$$

We insert this relation in (4) and project the result on $|\varphi_n\rangle$:

$$\begin{aligned} H_0 \sum_k c_k(t)|\varphi_k\rangle e^{-iE_k t/\hbar} \quad &+ \quad W(t) \sum_k c_k(t)|\varphi_k\rangle e^{-iE_k t/\hbar} \\ &= \quad i\hbar \frac{\partial}{\partial t} \sum_k c_k(t)|\varphi_k\rangle e^{-iE_k t/\hbar} \Rightarrow \end{aligned}$$

$$\begin{aligned} \sum_k c_k(t) E_k |\varphi_k\rangle e^{-iE_k t/\hbar} \quad &+ \quad \sum_k c_k(t) W(t) |\varphi_k\rangle e^{-iE_k t/\hbar} \\ = i\hbar \sum_k \frac{\partial c_k(t)}{\partial t} |\varphi_k\rangle e^{-iE_k t/\hbar} \quad &+ \quad i\hbar \sum_k c_k(t) |\varphi_k\rangle \left(-\frac{iE_k}{\hbar} \right) e^{-iE_k t/\hbar} \Rightarrow \end{aligned}$$

$$E_n c_n(t) e^{-iE_n t/\hbar} + \sum_k c_k(t) W_{nk}(t) e^{-iE_k t/\hbar} = i\hbar \frac{\partial c_n(t)}{\partial t} e^{-iE_n t/\hbar} + E_n c_n(t) e^{-iE_n t/\hbar} \Rightarrow$$

$$\sum_k c_k(t) W_{nk}(t) e^{-iE_k t/\hbar} = i\hbar \frac{\partial c_n(t)}{\partial t} e^{-iE_n t/\hbar} \Rightarrow$$

$$\frac{\partial c_n(t)}{\partial t} = \frac{1}{i\hbar} \sum_k c_k(t) W_{nk}(t) e^{i\omega_{nk} t} \tag{6}$$

where
,$W_{nk} = \langle\varphi_n|W(t)|\varphi_k\rangle$, the perturbation matrix element
,$\omega_{nk} = (E_n - E_k)/\hbar$

Up to this point we have made no approximation. The difficulty in solving (6) arises from the fact that the coefficients are expressed in terms of themselves. In order to evaluate the coefficients from (6) we make two assumptions:

1. The system is initially in state $|i\rangle$, thus, all of the coefficients at t=0 are equal to zero, except for $c_i : c_j(t = 0) = \delta_{ij}$
2. The perturbation is very weak and applied for a short period of time, such that all of the coefficients remain nearly unchanged.

With these in mind, (6) gives us:

$$\frac{\partial c_n(t)}{\partial t} = \frac{1}{i\hbar} c_i(t) W_{ni}(t) e^{i\omega_{ni} t} \tag{7}$$

so for any final state the coefficient will be $(c_f(t) \approx c_f(0) = 0)$:

$$c_f(t) = \frac{1}{i\hbar}\int_0^t W_{fi}(t')e^{i\omega_{fi}t'}dt' \tag{8}$$

REMARKS

In order to derive (8) we forced all of the coefficients of the states to remain virtually unchanged, at time t, from the values they initially had (t=0). For that we must pay a price. Equation (8) holds only for perturbations that last a very short period of time, i.e. that don't have enough time to significantly alter the state of the system.

Also, by zeroing out the coefficients of states in (6) we deprived the system of any capability of reaching the final state by alternate routes, i.e. only direct transitions from state $|i\rangle$ to $|f\rangle$ are possible.

We have extensively used frases that refer to transitions between *eigenstates* of the unperturbed hamiltonian H_0. Such frases are commonplace in Quantum Mechanics literature[1] but are also a point of much controversy and discussions. The controversy has to do mainly with the interpretation one gives to the mathematical results of Quantum Mechanics. As an example of the situation a quotation is given from the very well known and accepted book *Quantum Mechanics*, by L. E. Ballentine[5, p. 351] (who supports[6] an interpretation for the wavefunction other than the *orthodox* interpretation):

> "When problems of this sort are discussed formally, it is common to speak of the perturbation as causing *transitions* between the eigenstates H_0. If this means only that the system has absorbed from the perturbing field (or emitted to it) the energy difference $\hbar\omega_{fi} = \epsilon_f - \epsilon_i$, and so has changed its energy, there is no harm in such language. But if the statement is interpreted to mean that the state has changed from its initial value of $|\Psi(0)\rangle = |i\rangle$ to a final value of $|\Psi(T)\rangle = |f\rangle$, then it is incorrect.
>
> ...
>
> If the state vector $|\Psi\rangle$ is of the form (5) it is correct to say that the probability of the energy being ϵ_f is $|c_f|^2$. In the formal notation this becomes $Prob(E = \epsilon_f|\Psi) = |\alpha_f|^2$, which is a correct formula of quantum theory. But it is nonsense to speak of the probability of the state being $|f\rangle$ when in fact the state is $|\Psi\rangle$."

The application of the perturbation changes the state of the system from the initial state $|\varphi_i\rangle$ to a final state $|\varphi_f\rangle$, both of which are eigenstates of

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[1] This language is used by Cohen-Tannoudji, Atkins, Merzbacher [1, 2, 3, 4] and many more.

the unperturbed hamiltonian H_0. The probability of finding the system in the eigenstate $|\varphi_f\rangle$ is:

$$\mathscr{P}_{if}(t) = |\langle\varphi_f|\psi(t)\rangle|^2 \tag{9}$$

Using (8) we have:

$$\boxed{\mathscr{P}_{if}(t) = \tfrac{1}{\hbar^2}\left|\int_0^t e^{i\omega_{fi}t'} W_{fi}(t')dt'\right|^2} \tag{10}$$

3. High frequency harmonic perturbation

The case of an oscillating (i.e. harmonic) perturbation is a most important one. Once the effects of an oscillating perturbation are known then the general case can be evaluated since an arbitrary perturbation can be expressed as a superposition of harmonic functions. An example of an oscillating perturbation is an electromagnetic wave such as a laser pulse.

We define the oscillating perturbation having the form:

$$W(t) = 2W cos(\omega t) = W\left(e^{i\omega t} + e^{-i\omega t}\right) \tag{11}$$

Inserting this in (8) we obtain:

$$\begin{aligned} c_f(t) &= \frac{W_{fi}}{i\hbar}\int_0^t \left(e^{i\omega t'} + e^{-i\omega t'}\right) e^{i\omega_{fi}t'}dt' \\ &= \frac{W_{fi}}{i\hbar}\left\{\frac{e^{i(\omega_{fi}+\omega)t}-1}{i(\omega_{fi}+\omega)} + \frac{e^{i(\omega_{fi}-\omega)t}-1}{i(\omega_{fi}-\omega)}\right\} \end{aligned} \tag{12}$$

Thus, equation (10) becomes:

$$\mathscr{P}_{if}(t) = \frac{W_{fi}^2}{\hbar^2}\left|\frac{e^{i(\omega_{fi}+\omega)t}-1}{i(\omega_{fi}+\omega)} + \frac{e^{i(\omega_{fi}-\omega)t}-1}{i(\omega_{fi}-\omega)}\right|^2 \tag{13}$$

At this point we make an approximation assuming that the oscillating angular frequency of the perturbation has a value near the Bohr angular frequency of $|\varphi_i\rangle$ and $|\varphi_f\rangle$, ω_{fi}:

$$\omega \simeq \omega_{fi}$$

which can also be written:

$$|\omega - \omega_{fi}| \ll |\omega_{fi}|$$

With this approximation, the first term in equation (13) becomes negligible compared to the second one. This is made obvious from the fact that the exponential factor ($e^{ix} = cosx + isinx$) cannot become greater than 1. Thus, the prominent term is defined by the denominator. When $\omega \simeq \omega_{fi}$ (usualy of high frequency $\omega_{fi} \approx 10^{15} sec^{-1}$) the denominator of the second term goes to zero (the situation is reversed when $\omega \simeq -\omega_{fi}$, so we need not examine this case separately).

The second term (also called the "resonant term") can be written:

$$\begin{aligned} A_- &= \frac{e^{i(\omega_{fi}-\omega)t} - 1}{i(\omega_{fi} - \omega)} \\ &= e^{i(\omega_{fi}-\omega)t/2} \frac{e^{i(\omega_{fi}-\omega)t/2} - e^{-i(\omega_{fi}-\omega)t/2}}{i(\omega_{fi} - \omega)} \\ &= e^{i(\omega_{fi}-\omega)t/2} \frac{sin[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)/2} \end{aligned} \tag{14}$$

Thus, the probability becomes:

$$\mathscr{P}_{if}(t) = \frac{W_{fi}^2}{\hbar^2} \left| \frac{sin[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)/2} \right|^2 \tag{15}$$

and, by introducing the function $F(t, \omega - \omega_{fi})$:

$$F(t, \omega - \omega_{fi}) = \left\{ \frac{sin[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)/2} \right\}^2 \tag{16}$$

we obtain:

$$\mathscr{P}_{if}(t) = \frac{W_{fi}^2}{\hbar^2} F(t, \omega - \omega_{fi}) \tag{17}$$

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As we can see in the figure (1) the function $F(t, \omega)$ has a sharp peak about the central angular frequency ω. Do to this behavior we say that F, and thus the probability $\mathscr{P}_{if}(t; \omega)$, shows a *resonant* nature. The distance between the first two zeros are defined as the resonance width $\Delta\omega$. The area underlined by $\mathscr{P}_{if}(t; \omega)$ at this interval is over 95% of the total area. For $\Delta\omega$ we have:

$$\Delta\omega \simeq \frac{4\pi}{t} \tag{18}$$

The function $F(t, \omega)$ appears in equation (17) with an offset. As a result, the resonant point is located at $\omega = \omega_{fi}$. The modulus of the resonant term in equation (13), $|A_-|^2$, behaves in the same manner. In the antiresonant case, $|A_+|^2$, the resonant point is located at $\omega = -\omega_{fi}$. Placing both of these functions on the same graph it becomes clear that the part of $|A_+|^2$

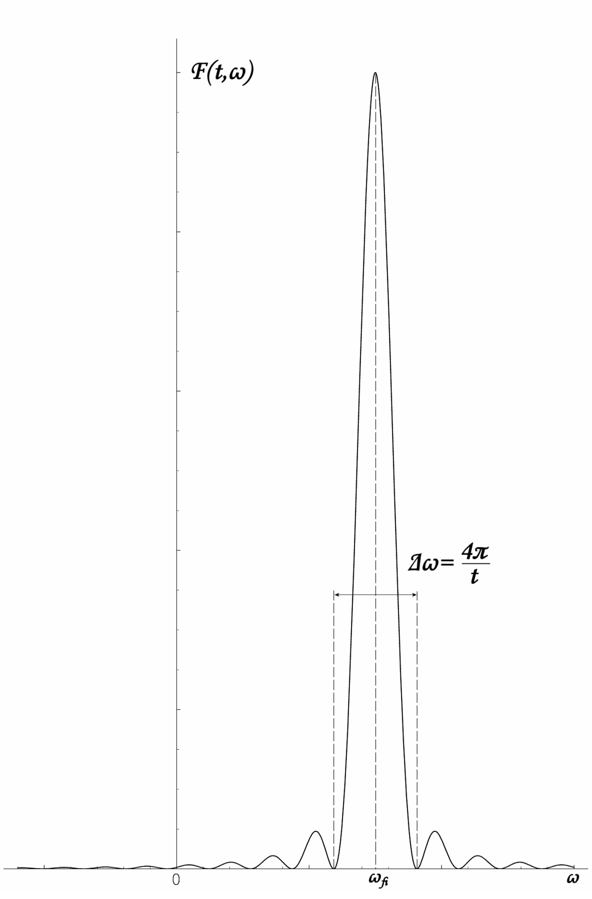

Figure 1: The function $F(t, \omega)$ shows a resonant nature.

that reaches ω_{fi} is the diffraction pattern (negligible). In view of this, the resonant approximation is justified when $|A_+|^2$ and $|A_-|^2$ are far apart:

$$2|\omega_{fi}| \gg \Delta\omega \tag{19}$$

and with (18), we obtain:

$$t \gg \frac{1}{|\omega_{fi}|} \simeq \frac{1}{\omega} \tag{20}$$

Another point noteworthy is the behavior of the probability function at resonance. From equation (17) at the resonant frequency we have

$$\mathscr{P}_{if}(t; \omega = \omega_{fi}) = \frac{W_{fi}^2}{\hbar^2} t^2 \tag{21}$$

from which we acquire probability values greater than one for large values of t. For this equation to have physical meaning the probability $\mathscr{P}_{if}$ must be less than 1, which we have when:

$$t \ll \frac{\hbar}{|W_{fi}|} \tag{22}$$

and using, (20):

$$\frac{1}{|\omega_{fi}|} \ll \frac{\hbar}{|W_{fi}|} \tag{23}$$

which we can read as: the matrix element of the perturbation must be much smaller than the energy separation between the initial and final states.

4. Quantum jumps to the continuum

When the final state is part of a continuum of states (i.e. when the energy belongs to a continuous part of the spectrum of H_0) we must account for all the states to which the system can jump to. This is done by integrating the probability as given by equation (17) with the *density of states* $\rho(E)$ as weights:

$$\mathscr{P}(t) = \int_{\{E_{acc}\}} \mathscr{P}_{if}(t)\rho(E)dE \tag{24}$$

,where $\{E_{acc}\}$ denotes all the states that the system can jump to under the influence of the perturbation.
(What we have actually done is create a probability density from the probability equation).

The probability function is sharply peaked at $\omega = \omega_{fi}$ and as a result acts as a delta function in the integral and thus selects the value for the density function at $\omega = \omega_{fi}$. By substituting equation (17) in (24) we have:

$$\begin{aligned} \mathscr{P}(t) &= \int_{\{E_{acc}\}} \frac{W_{fi}^2}{\hbar^2} F(t, \omega - \omega_{fi})\rho(E)dE \\ &= \int_{\{E_{acc}\}} \frac{W_{fi}^2}{\hbar^2} \left\{ \frac{sin[(\omega_{fi} - \omega)t/2]}{(\omega_{fi} - \omega)/2} \right\}^2 \rho(E)dE \end{aligned}$$

as shown in the figure (2) the range of energies is very narrow and as a result the matrix element W_{fi} and the density of states $\rho(E)$ can be considered as constant:

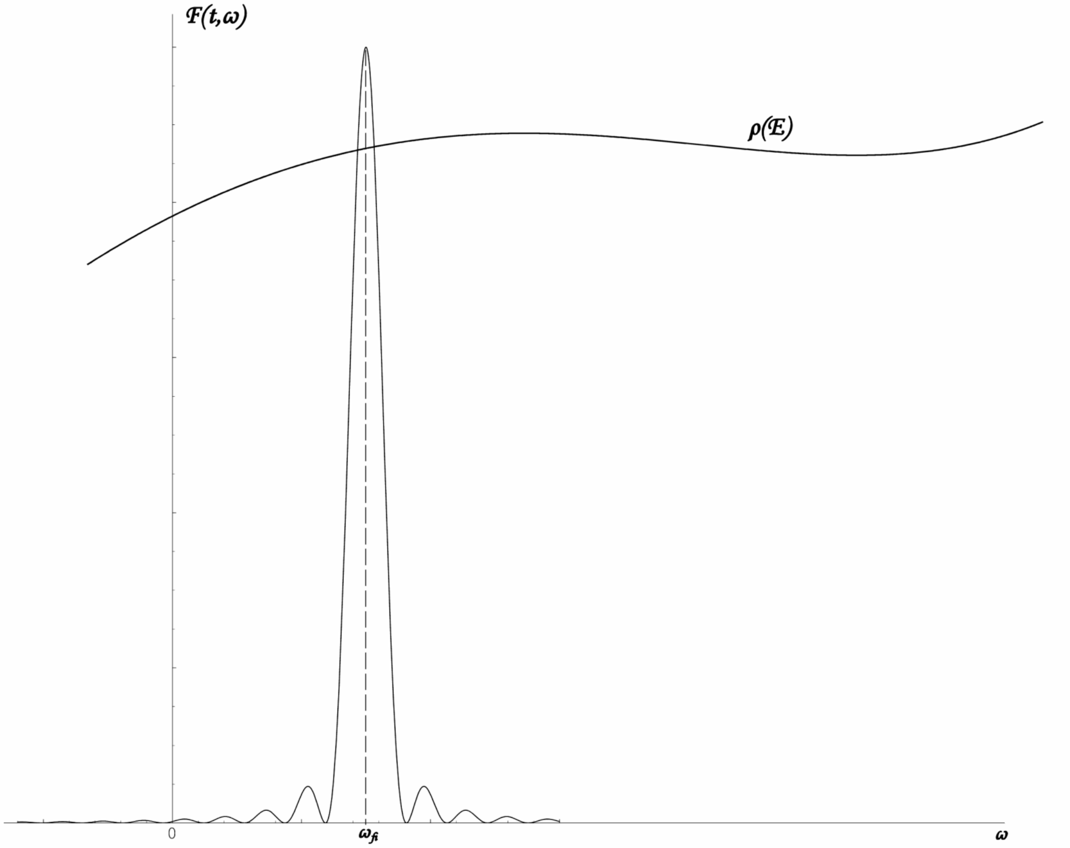

Figure 2: The function $F(t,\omega)$ acts as a delta function.

$$\begin{aligned}
\mathscr{P}(t) &= \frac{W_{fi}^2}{\hbar^2}\rho(E_{fi})\int_{\{E_{acc}\}}\left\{\frac{sin[(\omega_{fi}-\omega)t/2]}{(\omega_{fi}-\omega)/2}\right\}^2 dE \\
&= \frac{W_{fi}^2}{\hbar^2}\rho(E_{fi})\int_{\{E_{acc}\}}\left\{\frac{sin[(\omega_{fi}-\omega)t/2]}{(\omega_{fi}-\omega)/2}\right\}^2 \hbar d\omega \\
&= \frac{W_{fi}^2}{\hbar^2}\rho(E_{fi})\hbar\left(\frac{2}{t}\right)t^2\int_{-\infty}^{+\infty}\frac{sin^2 x}{x^2}dx
\end{aligned}$$

where we substituted $E=\hbar\omega$, $x=(\omega_{fi}-\omega)t/2$ and used the fact that for frequencies far from ω_{fi} the function $sin^2 x/x^2$ is negligible so we can extend the limits to infinity. The value for the integral is well known and equal to π, thus we obtain:

$$\mathscr{P}(t) = \frac{2\pi}{\hbar} W_{fi}^2 \rho(E_{fi}) t \tag{25}$$

The result is significant in that the probability has a linear dependence in time. The *transition rate* is:

$$\boxed{\mathscr{W} = \frac{d\mathscr{P}(t)}{dt} = \frac{2\pi}{\hbar} W_{fi}^2 \rho(E_{fi})} \tag{26}$$

This result is known as *Fermi's Golden Rule.* This equation states that in order to calculate the transition rate all we have to do is multiply the square modulus of the perturbation matrix element between the two states, by the the density of states at the transition frequency.

Bibliography

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