

Chapter 8

TIME DEPENDENT PERTURBATIONS: TRANSITION THEORY

8.1 General Considerations

The methods of the last chapter have as their goal expressions for the exact energy eigenstates of a system in terms of those of a closely related system to which a constant perturbation has been applied. In the present chapter we consider a related problem, namely, that of determining the rate at which transitions occur between energy eigenstates of a quantum system of interest as a result of a time-dependent, usually externally applied, perturbation. Indeed, it is often the case that the only way of experimentally determining the structure of the energy eigenstates of a quantum mechanical system is by perturbing it in some way. We know, e.g., that if a system is in an eigenstate of the Hamiltonian, then it will remain in that state for all time. By applying perturbations, however, we can induce transitions between different eigenstates of the unperturbed Hamiltonian. By probing the rate at which such transitions occur, and the energies absorbed or emitted by the system in the process, we can infer information about the states involved. The calculation of transition rates for such situations, and a number of others of practical interest are addressed in this chapter.

To begin, we consider a system described by time-independent Hamiltonian H_0 to which a time-dependent perturbation $\hat{V}(t)$ is applied. Thus, while the perturbation is acting, the total system Hamiltonian can be written

$$H(t) = H_0 + \hat{V}(t). \quad (8.1)$$

It will be implicitly assumed unless otherwise stated in what follows that the perturbation $\hat{V}(t)$ is small compared to the unperturbed Hamiltonian H_0 ; if we want to study the eigenstates of H_0 we do not want to change those eigenstates drastically by applying a strong perturbation. In fact, we will often write the perturbation of interest in the form

$$\hat{V}(t) = \lambda V(t) \quad (8.2)$$

where λ is a smallness parameter that we can use to tune the strength of \hat{V} . We will denote by $\{|n\rangle\}$ a complete ONB of eigenstates of H_0 with unperturbed energies ε_n , so that, by assumption

$$H_0|n\rangle = \varepsilon_n|n\rangle \quad \sum_n |n\rangle\langle n| = 1 \quad \langle n|n'\rangle = \delta_{n,n'}. \quad (8.3)$$

Our general goal is to calculate the amplitude (or probability) to find the system in a given final state $|\psi_f\rangle$ at time t if it was known to be in some other particular state $|\psi_i\rangle$ at time $t = t_0$. Implicit in this statement is the idea that we are going to let the system evolve from $|\psi_i\rangle$ until time t and then make a measurement of an observable A of which $|\psi_f\rangle$ is an eigenstate (e.g., we might be measuring the operator $P_f = |\psi_f\rangle\langle\psi_f|$). A little less generally, if the system was initially in the unperturbed eigenstate $|n_i\rangle$ of H_0 at t_0 ,

we wish to find the amplitude that it will be left in (or will be found to have made a transition to) the eigenstate $|n_f\rangle$ at time $t > t_0$, where now the measurement will be that of the unperturbed Hamiltonian itself. We note in passing that if we could solve the full Schrödinger equation

$$i\hbar \frac{d}{dt} |\psi_i(t)\rangle = H(t) |\psi_i(t)\rangle \quad (8.4)$$

for the initial condition $|\psi_i(t_0)\rangle = |\psi_i\rangle$ of interest, the solution to the general problem would be immediate. The corresponding transition amplitude would then just be the inner product $T_{i \rightarrow f}(t) = \langle \psi_f | \psi_i(t) \rangle$ and the transition probability would be

$$W_{i \rightarrow f} = |T_{i \rightarrow f}|^2 = |\langle \psi_f | \psi_i(t) \rangle|^2 = \langle \psi_i(t) | \psi_f \rangle \langle \psi_f | \psi_i(t) \rangle. \quad (8.5)$$

It is useful, in what follows, to develop our techniques for solving time-dependent problems of this kind in terms of the evolution operator $U(t, t_0)$, or propagator, which evolves the system over time

$$|\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle.$$

We recall a few general features of the evolution operator

1. It is Unitary, i.e.,

$$U^\dagger(t, t_0) = U^{-1}(t, t_0) = U(t_0, t). \quad (8.6)$$

2. It obeys a simple composition rule

$$U(t, t_0) = U(t, t') U(t', t_0). \quad (8.7)$$

3. It is smoothly connected to the identity operator

$$\lim_{t \rightarrow t'} U(t, t') = 1. \quad (8.8)$$

4. It obeys an operator form of the Schrödinger equation

$$i\hbar \frac{d}{dt} U(t, t_0) = H(t) U(t, t_0). \quad (8.9)$$

5. If $H(t) = H_0$ is independent of time, then the evolution operator takes a particularly simple form, i.e.,

$$U = U_0(t, t_0) = e^{-iH_0(t-t_0)/\hbar}. \quad (8.10)$$

By comparison with what we have written above, the transition amplitude $T_{i \rightarrow f}$ can be expressed as the matrix element of the evolution operator between the initial and final states, i.e.,

$$T_{i \rightarrow f} = \langle \psi_f | \psi_i(t) \rangle = \langle \psi_f | U(t, t_0) | \psi_i \rangle, \quad (8.11)$$

or, if we are interested in transitions between eigenstates of H_0 , we have

$$T_{n \rightarrow m} = \langle m | U(t, t_0) | n \rangle \quad W_{n \rightarrow m} = |\langle m | U(t, t_0) | n \rangle|^2 \quad (8.12)$$

Typically, of course, it is the presence of the perturbation $\hat{V}(t)$ that renders the full Schrödinger equation intractable. Indeed, when $\lambda = 0$, each eigenstate of H_0 evolves so as to acquire an oscillating phase

$$U_0(t, t_0) | n \rangle = e^{-i\omega_n(t-t_0)} | n \rangle \quad (8.13)$$

but no transitions between different eigenstates occur:

$$W_{nm} = \delta_{nm}.$$

It is the perturbation $\hat{V}(t)$ that allows the system to evolve into a mixture of unperturbed states, an evolution that is viewed as inducing transitions between them.

Our goal, then, is to develop a general expansion for the full evolution operator $U(t, t_0)$ in powers of the perturbation, or equivalently, in powers of the small parameter λ . To this end, it is useful to observe that the unperturbed evolution of the system is not the goal of our calculation, involving as it does all of the unperturbed eigenenergies of the system. Indeed, that problem is assumed to have been completely solved. It would be convenient, therefore, to transform to a set of variables that evolve, in a certain sense, along with the unperturbed system, so that we can focus on the relatively slow part of the evolution induced by the weak externally applied perturbation, without worrying about all the rapid oscillation of the phase factors associated with the evolution occurring under H_0 . The idea here is similar to transforming to a rotating coordinate system to ease the solution of simple mechanical problems. In the present context, we expect that in the presence of a small perturbation the unperturbed evolution changes from the form given above into a mixture of different states, which we can generally write in the form

$$U(t, t_0)|n\rangle = \sum_m \phi_m(t) e^{-i\varepsilon_m(t-t_0)/\hbar} |m\rangle \quad (8.14)$$

where for small enough λ the expansion coefficients $\phi_m(t)$ are, it is to be hoped, slowly varying relative to the rapidly oscillating phase factors associated with the unperturbed evolution. As suggested above, we can formally eliminate this fast evolution generated by H_0 by working in the so-called “interaction picture”.

Recall that our axioms of quantum mechanics were developed in the Schrodinger picture in which the state of the system evolves in time

$$|\psi_{Sch}(t)\rangle = U(t, t_0)|\psi(t_0)\rangle \quad (8.15)$$

while fundamental observables of the system are associated with time-independent Hermitian operators $A = A_{Sch}$. By contrast, it is possible to develop a different formulation of quantum mechanics, the so-called Heisenberg picture, in which the state of the system

$$|\psi_H(t)\rangle = |\psi(t_0)\rangle = U^+(t, t_0)|\psi_{Sch}(t)\rangle \quad (8.16)$$

remains fixed in time, but observables are associated with time-evolving operators

$$A_H(t) = U^+(t, t_0)A_{Sch}U(t, t_0). \quad (8.17)$$

The kets and operators of one picture are related to those of the other through the unitary transformation induced by the evolution operator $U(t, t_0)$ and its adjoint, and preserve the mean values, and hence predictions, of quantum mechanics in the process.

In this same spirit, it is possible to develop a formulation in which some of the time evolution is associated with the kets of the system and some of it associated with the operators of interest. An *interaction picture* of this sort can be defined for any system in which the Hamiltonian can be written in the form $H = H_0 + V(t)$, with the state vector of this picture

$$|\psi_I(t)\rangle = U_0^+(t, t_0)|\psi_{sch}(t)\rangle \quad (8.18)$$

being defined relative to that of the Schrödinger picture through the *inverse* of the unitary transformation

$$U_0(t, t_0) = \exp[-iH_0(t - t_0)/\hbar] \quad (8.19)$$

which governs the system in the absence of the perturbation. This form for the state vector suggests that the inverse (or adjoint) operator U^+ acts on the fully-evolving state vector of the Schrödinger picture to “back out” or undo the fast evolution associated with the unperturbed part of the Hamiltonian. In a similar fashion, the operators

$$A_I(t) = U_0^+(t, t_0)A_{Sch}(t)U_0(t, t_0), \quad (8.20)$$

of the interaction picture are related to those of the Schrodinger picture through the same corresponding unitary transformation, but as applied to operators (we have included a time dependence in the Schrodinger operator $A_{Sch}(t)$ on the right to take into account any intrinsic time dependence exhibited by such operators, as occurs, e.g., with a sinusoidally applied perturbing field).

Naturally, we can define an evolution operator $U_I(t, t_0)$ for the interaction picture that evolves the state vector $|\psi_I(t)\rangle$ in time, according to the relation

$$|\psi_I(t)\rangle = U_I(t, t_0)|\psi_I(t_0)\rangle \quad (8.21)$$

Using the definitions given above we deduce that

$$U_I(t, t_0) = U_0^+(t, t_0)U(t, t_0) \quad (8.22)$$

or, multiplying this last equation through by $U_0(t, t_0)$, we obtain a result for the full evolution operator

$$U(t, t_0) = U_0(t, t_0)U_I(t, t_0). \quad (8.23)$$

in terms of the evolution operators U_0 and U_I .

To obtain information about transitions between the unperturbed eigenstates of H_0 , then, we need the transition amplitudes

$$T_{n \rightarrow m} = \langle m|U(t, t_0)|n\rangle = \langle m|U_0(t, t_0)U_I(t, t_0)|n\rangle = e^{-i\omega_m(t-t_0)}\langle m|U_I(t, t_0)|n\rangle \quad (8.24)$$

and transition probabilities

$$W_{n \rightarrow m} = |T_{n \rightarrow m}|^2 = |\langle m|U_I(t, t_0)|n\rangle|^2. \quad (8.25)$$

We see, therefore, that the evolution operator of the interaction picture does indeed contain all information about transitions induced between the unperturbed eigenstates. The evolution equation obeyed by $U_I(t, t_0)$ is also straightforward to obtain. By taking derivatives of $U(t, t_0)$ we establish (with t_0 fixed) that

$$\frac{dU}{dt} = \frac{dU_0}{dt}U_I + U_0\frac{dU_I}{dt}. \quad (8.26)$$

But clearly

$$\frac{dU}{dt} = \frac{-i}{\hbar}[H_0 + \hat{V}(t)]U = \frac{-i}{\hbar}[H_0 + \hat{V}(t)]U_0U_I \quad (8.27)$$

and

$$\frac{dU_0}{dt} = \frac{-i}{\hbar}H_0U_0. \quad (8.28)$$

From these last three equations we deduce that

$$i\hbar\frac{dU_I}{dt} = U_0^+\hat{V}(t)U_0U_I \quad (8.29)$$

which we can write as

$$i\hbar\frac{dU_I}{dt} = \hat{V}_I(t)U_I. \quad (8.30)$$

Thus, the evolution operator in the interaction picture evolves under a Schrödinger equation that is governed by a Hamiltonian

$$\hat{V}_I(t) = U_0^+ \hat{V}(t) U_0 \quad (8.31)$$

that only includes the perturbing part of the Hamiltonian (the interaction), as represented in this picture. Since $U_I(t, t_0)$ shares the limiting behavior

$$\lim_{t \rightarrow t_0} U_I(t, t_0) = \lim_{t \rightarrow t_0} U_0^+(t, t_0) U(t, t_0) = 1 \quad (8.32)$$

of any evolution operator, it obeys the integral equation that we derived earlier for evolution operators governed by a time-dependent Hamiltonian, i.e.,

$$U_I(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t dt' \hat{V}_I(t') U_I(t', t_0) \quad (8.33)$$

and hence can be expanded in the same way in powers of the perturbation, i.e.,

$$U_I(t, t_0) = \sum_{k=0}^{\infty} U_I^{(k)}(t, t_0) \quad (8.34)$$

where

$$\begin{aligned} U_I^{(k)}(t, t_0) &= \left(\frac{1}{i\hbar} \right)^k \int_{t_0}^t dt_k \cdots \int_{t_0}^{t_2} dt_1 \hat{V}_I(t_k) \hat{V}_I(t_{k-1}) \cdots \hat{V}_I(t_1) \\ &= \left(\frac{1}{i\hbar} \right)^k \int_{t_0}^t dt_k \cdots \int_{t_0}^{t_2} dt_1 U_0(t, t_k) \hat{V}(t_k) U_0(t_k, t_{k-1}) \hat{V}(t_{k-1}) \cdots \\ &\quad \cdots \hat{V}(t_2) U_0(t_2, t_1) \hat{V}(t_1) \end{aligned} \quad (8.35)$$

Combining this with (8.23) it is possible to deduce a similar expansion

$$U(t, t_0) = \sum_{k=0}^{\infty} U^{(k)}(t, t_0) \quad (8.36)$$

$$\begin{aligned} U^{(k)}(t, t_0) &= \left(\frac{1}{i\hbar} \right)^k \int_{t_0}^t dt_k \cdots \int_{t_0}^{t_2} dt_1 U_0(t, t_k) \hat{V}(t_k) U_0(t_k, t_{k-1}) \hat{V}(t_{k-1}) \cdots \\ &\quad \cdots \hat{V}(t_2) U_0(t_2, t_1) \hat{V}(t_1) U_0(t_1, t_0) \end{aligned} \quad (8.37)$$

for the full evolution operator. Note the structure of this is of a sum (integral) over all processes whereby the system evolves under H_0 without perturbation from t_0 to t_1 , at which time it is acted upon by the perturbation $\hat{V}(t_1)$, then evolves without perturbation from t_1 to t_2 , at which time it is acted upon by the perturbation $\hat{V}(t_2)$, and so on. The k th order contribution arises from all those those processes in which the system is scattered (or perturbed) exactly k times between t_0 and t , with the particular times at which those perturbations could have acted being integrated over. It is this structure that forms the basis for diagrammatic representations for the perturbation process, such as those introduced in the context of electrodynamics by Feynman.

If the perturbation is small enough, this formal expansion for the propagator of the system can be truncated after the first order term, and as such allows us to address in a perturbative sense the problem originally posed. For example, if the system is at

$t = t_0$ initially in an eigenstate $|\psi(t_0)\rangle = |n\rangle$ of the unperturbed Hamiltonian, the results of the above expansion reveal that the state of the system at time t will be given by the expansion

$$|\psi(t)\rangle = \sum_m \psi_m(t)|m\rangle \quad (8.38)$$

where

$$\begin{aligned} \psi_m(t) &= \langle m|U(t, t_0)|\psi(t_0)\rangle = \langle m|U(t, t_0)|n\rangle \\ &= \langle m|U_0(t, t_0)U_I(t, 0)|n\rangle = e^{-i\omega_m(t-t_0)}\langle m|U_I(t, t_0)|n\rangle. \end{aligned} \quad (8.39)$$

Truncating the expression for U_I at first order

$$U_I(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t dt' \hat{V}_I(t'). \quad (8.40)$$

and inserting the result into the expression for ψ_m , keeping the lowest-order non-zero result for each coefficient, we obtain a basic equation of time-dependent perturbation theory:

$$\psi_m(t) = e^{-i\omega_m(t-t_0)} \left[\delta_{n,m} - \frac{i}{\hbar} \int_{t_0}^t dt' V_{mn}(t') e^{i\omega_{mn}(t'-t_0)} \right] \quad (8.41)$$

where $\omega_{mn} = \omega_m - \omega_n$ is the Bohr frequency associated with the transition between levels n and m . Clearly in this last expression, the first term, involving the Kronecker delta function is associated with the amplitude for the system to be found in the initial state, while the remaining terms give the desired (first-order) transition amplitudes

$$T_{n \rightarrow m} = -\frac{i}{\hbar} e^{-i\omega_m(t-t_0)} \int_{t_0}^t dt' V_{mn}(t') e^{i\omega_{mn}(t'-t_0)} \quad (8.42)$$

from which follow the corresponding transition probabilities

$$W_{n \rightarrow m} = \hbar^{-2} \left| \int_{t_0}^t dt' V_{mn}(t') e^{i\omega_{mn}t'} \right|^2. \quad (8.43)$$

For a perturbation that starts in the far distant past and disappears in the far distant future, these results reduce to a particularly simple form, in which the total transition probability can be written

$$W_{n \rightarrow m} = \hbar^{-2} \left| \int_{-\infty}^{\infty} dt' V_{mn}(t') e^{i\omega_{mn}t'} \right|^2 = \frac{2\pi}{\hbar^2} \left| \tilde{V}_{mn}(\omega_{mn}) \right|^2 \quad (8.44)$$

where

$$\tilde{V}_{mn}(\omega_{mn}) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dt' V_{mn}(t') e^{i\omega_{mn}t'} \quad (8.45)$$

is simply the Fourier transform of the perturbing matrix element connecting the two states involved in the transition, evaluated at a frequency ω_{mn} corresponding to the energy difference between the two states involved.

As an example, we consider a 1D harmonic oscillator

$$H_0 = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 X^2 \quad (8.46)$$

which is initially (at $t = -\infty$) in its ground state when a perturbing electric field pulse is applied of the form

$$\hat{V}(t) = -f(t)X. \quad (8.47)$$

In this expression, $f(t) = eE(t)$ represents the spatially uniform, but time-dependent force exerted by the field on the charged harmonically-bound particle. We might, e.g., example take a pulse envelope

$$f(t) = f_0 e^{-t^2/\tau^2} \quad (8.48)$$

with a Gaussian shape that peaks at a time that for convenience we have set equal to $t = 0$. Our goal is to find the the probability that the particle is left by this pulse in the n th excited state. Provided the pulse strength is sufficiently low, the transition probability can then be written

$$W_{0 \rightarrow n} = \frac{2\pi}{\hbar^2} \left| \tilde{V}_{n,0}(n\omega) \right|^2 \quad (8.49)$$

where

$$\tilde{V}_{n,0}(\omega) = \frac{X_{n,0}}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dt' f(t') e^{i\omega t'} \quad (8.50)$$

and

$$X_{n,0} = \langle n|X|0 \rangle = \sqrt{\frac{\hbar}{2m\omega}} \delta_{n,1}. \quad (8.51)$$

Clearly, the first-order transition amplitude vanishes except for the first excited state, i.e., $n = 1$. For the Gaussian pulse, evaluation of the Fourier integral leads to the result that long after the pulse has passed through, the probability for the charge to be excited to the $n = 1$ state is

$$W_{0 \rightarrow 1} = \frac{f_0^2 \pi \tau^2}{2m\hbar\omega} \exp(-\omega^2 \tau^2 / 2). \quad (8.52)$$

Note the transition probability becomes exponentially small as the duration of the pulse (as measured by the parameter τ) increases, and that there is a maximum in the transition probability as a function of τ . For this perturbative result to be valid, the strength f_0 of the field must be small enough that the transition probability $W_{0 \rightarrow 1}$ is small compared to unity.

8.2 Periodic Perturbations: Fermi's Golden Rule

An important class of problems involve perturbations that are harmonic in time, and expressible, therefore, in the form

$$\hat{V}(t) = [V e^{-i\omega t} + V^+ e^{i\omega t}] \theta(t). \quad (8.53)$$

Here, $\theta(t)$ is the Heaviside step function that describes the initial application of the perturbation at $t = 0$. Such a perturbation could describe, e.g., an electromagnetic wave applied to the system at $t = 0$, with a wavelength much large than the system size. We consider here the situation in which the perturbation is simply left on and calculate, after all the transients of the system have died down, the steady-state *transition rate*

$$\Gamma_{n \rightarrow m} = \lim_{t \rightarrow \infty} \frac{dW_{n \rightarrow m}}{dt} \quad (8.54)$$

which gives the number of transitions induced per unit time by the applied perturbation between an initial state $|n\rangle$ and a final state $|m\rangle$. Using our first order result (8.43), the transition probability for this situation can be written in the form

$$W_{n \rightarrow m}(t) = \frac{1}{\hbar^2} \left| \int_0^t [V_{mn} e^{i\Omega_+ t} + V_{nm}^* e^{i\Omega_- t}] dt \right|^2 \quad (8.55)$$

in which we have defined the quantities

$$\Omega_+ = \omega_m - \omega_n - \omega \quad (8.56)$$

and

$$\Omega_- = \omega_m - \omega_n + \omega.$$

Performing the integrals, we find

$$\begin{aligned} W_{n \rightarrow m}(t) &= \frac{1}{\hbar^2} \left| \frac{V_{mn} (e^{i\Omega_+ t} - 1)}{2i(\Omega_+/2)} + \frac{V_{nm}^* (e^{i\Omega_- t} - 1)}{2i(\Omega_-/2)} \right|^2 \\ &= \frac{1}{\hbar^2} \left| \frac{V_{mn} e^{i\Omega_+ t} \sin(\Omega_+ t/2)}{\Omega_+/2} + \frac{V_{nm}^* e^{i\Omega_- t} \sin(\Omega_- t/2)}{\Omega_-/2} \right|^2 \end{aligned} \quad (8.57)$$

which reduce to

$$\begin{aligned} W_{n \rightarrow m}(t) &= \frac{1}{\hbar^2} \left\{ |V_{nm}|^2 \frac{\sin^2(\Omega_+ t/2)}{(\Omega_+/2)^2} + |V_{nm}^*|^2 \frac{\sin^2(\Omega_- t/2)}{(\Omega_-/2)^2} \right\} \\ &+ \frac{2}{\hbar^2} \operatorname{Re} \left\{ e^{i\omega_{mn} t} V_{mn} V_{nm}^* \frac{\sin(\Omega_+ t/2)}{(\Omega_+/2)} \frac{\sin(\Omega_- t/2)}{(\Omega_-/2)} \right\}. \end{aligned} \quad (8.58)$$

To put this in a form useful for exploring the long time limit, we now multiply and divide the first two terms by $2\pi t$ and the last term by π^2 to obtain

$$\begin{aligned} W_{n \rightarrow m}(t) &= \frac{2\pi |V_{nm}|^2 t}{\hbar^2} \left\{ \frac{1}{\pi} \frac{\sin^2(\Omega_+ t/2)}{\Omega_+^2 t/2} + \frac{1}{\pi} \frac{\sin^2(\Omega_- t/2)}{\Omega_-^2 t/2} \right\} \\ &+ \frac{2\pi^2 |V_{mn} V_{nm}^*|}{\hbar^2} \left[\frac{1}{\pi} \frac{\sin(\Omega_+ t/2)}{(\Omega_+/2)} \right] \left[\frac{1}{\pi} \frac{\sin(\Omega_- t/2)}{(\Omega_-/2)} \right]. \end{aligned} \quad (8.59)$$

This form is convenient, because in the long time limit, the transient oscillations in the bracketed functions tend to die away, and they approach Dirac δ -functions as $T \rightarrow \infty$. Specifically, it is straightforward to establish the following representations of the Dirac δ -function

$$\delta(\omega) = \lim_{T \rightarrow \infty} \delta_1(T, \omega) = \lim_{T \rightarrow \infty} \frac{1}{\pi} \frac{\sin^2(\omega T/2)}{\omega^2 T/2} \quad (8.60)$$

$$\delta(\omega) = \lim_{T \rightarrow \infty} \delta_2(T, \omega) = \lim_{T \rightarrow \infty} \frac{1}{\pi} \frac{\sin(\omega T/2)}{\omega/2} \quad (8.61)$$

by showing that the functions $\delta(T, \omega)$ have, as $T \rightarrow \infty$, the appropriate limiting behavior (going to ∞ for $\omega = 0$, and going to 0 for $\omega \neq 0$, respectively), and that their integrals both approach unity for $T \rightarrow \infty$. This allows us to write, for times t much greater than typical evolution times of the unperturbed system

$$W_{n \rightarrow m}(t) = \frac{2\pi |V_{nm}|^2 t}{\hbar^2} \{ \delta(\Omega_+) + \delta(\Omega_-) \} + \frac{2\pi^2 |V_{mn} V_{nm}^*|}{\hbar^2} \delta(\Omega_+) \delta(\Omega_-). \quad (8.62)$$

Clearly, the product $\delta(\Omega_+) \delta(\Omega_-) = \delta(\omega_m - \omega_n + \omega) \delta(\omega_m - \omega_n - \omega)$ vanishes, since the δ -functions have different arguments. This leaves the first two terms, one of which must always vanish. If the final state has an energy greater than the initial, so that $\omega_m = \omega_n + \omega$, then the corresponding transition probability

$$W_{n \rightarrow m}(t) = \frac{2\pi |V_{nm}|^2 t}{\hbar^2} \delta(\omega_m - \omega_n - \omega) \quad (8.63)$$

describes the *resonant absorption* of a quantum $\Delta\varepsilon = \hbar\omega$ of energy; if the final state has a lower energy than the initial one, so that $\omega_m = \omega_n - \omega$, the transition probability

$$W_{n \rightarrow m}(t) = \frac{2\pi |V_{nm}|^2 t}{\hbar^2} \delta(\omega_m - \omega_n + \omega) \quad (8.64)$$

describes the *stimulated emission* of a quantum $\Delta\varepsilon = \hbar\omega$ of energy. The final form of the transition *rate* for these processes can then be written

$$\Gamma_{n \rightarrow m} = \frac{2\pi |V_{nm}|^2}{\hbar^2} \delta(\omega_m - \omega_n \pm \omega) = \frac{2\pi |V_{nm}|^2}{\hbar} \delta(\varepsilon_m - \varepsilon_n \pm \hbar\omega). \quad (8.65)$$

This is the simple form of what is referred to as *Fermi's golden rule*. Since the δ -functions makes the transition rate formally infinite or zero, this expression has meaning only when there is a distribution of final states having the right energy. Indeed, if we formally sum the transition rate $\Gamma_{n \rightarrow m}$ over all possible final states m , we can write the total transition probability in the form

$$\begin{aligned} \Gamma_n &= \sum_m \Gamma_{n \rightarrow m} = \sum_m \frac{2\pi}{\hbar} |V_{m,n}|^2 \delta(\varepsilon_m - \varepsilon_n \pm \hbar\omega) \\ &= \frac{2\pi}{\hbar} \int d\varepsilon \delta(\varepsilon - \varepsilon_n \pm \hbar\omega) \sum_m |V_{mn}|^2 \delta(\varepsilon - \varepsilon_m). \end{aligned} \quad (8.66)$$

If V_{mn} is approximately a constant over those states of the right energy to which transitions can occur, the integral simplifies and we end up with the second form of Fermi's golden rule

$$\Gamma_n = \frac{2\pi}{\hbar} |V_{mn}|^2 \rho(\varepsilon_n \pm \hbar\omega) = \frac{2\pi}{\hbar} |V_{mn}|^2 \rho(\varepsilon_f), \quad (8.67)$$

which involves the so-called *density of states*

$$\rho(\varepsilon) = \sum_m \delta(\varepsilon - \varepsilon_m) \quad (8.68)$$

evaluated at the final energy $\varepsilon_f = \varepsilon_n \pm \hbar\omega$ to which the transition can occur. Note that the density of states (or state distribution function) so defined has the property that

$$\int_{\varepsilon_1}^{\varepsilon_2} \rho(\varepsilon) d\varepsilon = N(\varepsilon_1, \varepsilon_2) \quad (8.69)$$

gives the number of states of the system with energies lying between ε_1 and ε_2 . Typically, situations in which Fermi's golden rule applies are those where the final set of states is part of a continuum (e.g., when a photon is given off or absorbed, so that there are a continuum of possible directions associated with the incoming or outgoing photon), and thus the density of states function $\rho(\varepsilon)$ is to be considered a continuous function of the final energy.

As an example of the application of Fermi's golden rule, and to see how densities of states of the sort typically encountered are constructed, we consider a ground state hydrogen atom, with a single bound electron described by the wave function

$$\psi_0(r) = (\pi a_0^3)^{-1/2} e^{-r/a_0}, \quad (8.70)$$

to which a harmonic perturbing potential

$$\hat{V}(\vec{r}, t) = V_0 \cos(\vec{k}_0 \cdot \vec{r} - \omega t), \quad (8.71)$$

is applied, in which V_0 is a constant having units of energy, and $\vec{k}_0 = k_0 \hat{z}$. (The form is clearly suggestive of an electromagnetic perturbation of some sort.) Assume that the perturbation causes ionizing transitions in which the initially bound electron ends up in a “free particle state” with final wavevector \vec{k} . We are interested in calculating the “differential ionization rate” $d\Gamma_0(\theta, \phi)/d\Omega$ for transitions to free-particle \vec{k} -states passing through an infinitesimal solid angle $d\Omega$ centered along some particular direction (θ, ϕ) . To proceed, we note that the perturbation can be written in the form

$$\hat{V}(t) = V e^{-i\omega t} + V^+ e^{i\omega t} \quad (8.72)$$

where

$$V = \frac{1}{2} V_0 e^{i\vec{k}_0 \cdot \vec{r}}. \quad (8.73)$$

From Fermi’s golden rule, irreversible transitions in which a quantum $\hbar\omega$ is absorbed (stimulated absorption) can only occur to states with final energies $\varepsilon_f = \varepsilon_i + \hbar\omega = \hbar\omega - \varepsilon_0$. This final energy is assumed to be associated with the final kinetic energy $\varepsilon_f = \hbar^2 k^2/2m$ of the ionized electron, which requires the final wavevector to have magnitude

$$k = k_f = \sqrt{\frac{2m(\hbar\omega - \varepsilon_0)}{\hbar^2}} = \sqrt{\frac{2m(\hbar\omega - me^4/2\hbar^2)}{\hbar^2}}. \quad (8.74)$$

The Fermi golden rule rate for transitions to a plane wave state of wavevector \vec{k} having this magnitude can be written

$$\Gamma_{0 \rightarrow \vec{k}} = \frac{2\pi}{\hbar} |V_{\vec{k},0}|^2 \delta(\varepsilon_k - \varepsilon_f) = \frac{2\pi}{\hbar} |V_{\vec{k},0}|^2 \delta(\varepsilon_k - \hbar\omega + \varepsilon_0) = \frac{2m\pi}{\hbar^3 k} |V_{\vec{k},0}|^2 \delta(k - k_f) \quad (8.75)$$

where we have used the result

$$\delta\left[\frac{\hbar^2}{2m}(k^2 - k_f^2)\right] = \frac{m}{\hbar^2 k} \delta(k - k_f). \quad (8.76)$$

Note that this last δ -function involves only the magnitude of the wavevector. The transition rate $d\Gamma_0(\theta, \phi)$ into all k -states passing through an infinitesimal solid angle $d\Omega$ along (θ, ϕ) is obtained by summing over all such final states, i.e.,

$$d\Gamma_0(\theta, \phi) = \frac{2m\pi}{\hbar^3 k} |V_{\vec{k},0}|^2 \sum_{\vec{k} \in d\Omega} \delta(k - k_f). \quad (8.77)$$

where the sum really is a symbolic way of writing an integral over all those wavevectors passing through the solid angle $d\Omega$ at (θ, ϕ) . Working in the spherical coordinate representation in k -space this can be written in the form

$$\sum_{\vec{k} \in d\Omega} \delta(k - k_f) = \int_0^\infty dk k^2 d\Omega \rho(\vec{k}) \delta(k - k_f) \quad (8.78)$$

where $\rho(\vec{k}) = \rho(k, \theta, \phi)$ is the density of plane wave states with wavevector \vec{k} , i.e., the number of states per unit volume of k -space. To obtain this quantity, it is convenient in problems of this sort to take the entire system to be contained in a large box of edge L , with normalized plane wave states

$$\langle \vec{r} | \vec{k} \rangle = \phi_{\vec{k}}(\vec{r}) = L^{-3/2} e^{i\vec{k} \cdot \vec{r}} \quad (8.79)$$

that satisfy periodic boundary conditions at the edges of the box. The allowed wavevectors in this situation are then of the form

$$\vec{k} = \frac{2\pi}{L}(n_x\hat{i} + n_y\hat{j} + n_z\hat{k}) \quad (8.80)$$

where n_x, n_y , and n_z are integers. The points in k -space thus form a regular cubic lattice with edge length $2\pi/L$, so there is exactly one state in every k -space unit cell volume of $(2\pi/L)^3$. The resulting density of states in k space

$$\rho(\vec{k}) = \left(\frac{L}{2\pi}\right)^3 \quad (8.81)$$

is uniform, therefore, independent of \vec{k} . Thus, the density of “ionized” states along $d\Omega$ takes the form

$$\sum_{k' \in d\Omega} \delta(k' - k) = \int_0^\infty dk k^2 d\Omega \rho(\vec{k}) \delta(k - k_f) = \left(\frac{L}{2\pi}\right)^3 k^2 d\Omega. \quad (8.82)$$

Putting this into the expression given above for $d\Gamma_0(\theta, \phi)$, and dividing through by $d\Omega$, we obtain the following expression for the “differential ionization rate”

$$\frac{d\Gamma_0(\theta, \phi)}{d\Omega} = \frac{2m\pi k}{\hbar^3} |V_{\vec{k},0}|^2 \rho(\vec{k}) d\Omega = \frac{mL^3 k}{4\pi^2 \hbar^3} |V_{\vec{k},0}|^2 \quad (8.83)$$

where it is understood at this point that $|\vec{k}| = k_f$ as given above. This quantity gives the number of transitions per unit time per unit solid angle along the specified direction. To complete the calculation we need to evaluate the matrix element

$$\begin{aligned} V_{\vec{k},0} &= \langle \vec{k} | V | \psi_0 \rangle = \frac{V_0}{2L^{3/2}} \int d^3r e^{-i\vec{k}\cdot\vec{r}} e^{i\vec{k}_0\cdot\vec{r}} \psi_0(r) \\ &= \frac{V_0}{2L^{3/2}} \int d^3r e^{-i(\vec{k}-\vec{k}_0)\cdot\vec{r}} \psi_0(r) = \frac{V_0}{2L^{3/2}} \tilde{\psi}_0(\vec{k} - \vec{k}_0) \end{aligned} \quad (8.84)$$

where, after a little hard work we find that

$$\tilde{\psi}_0(\vec{q}) = \frac{1}{\sqrt{\pi a_0^3}} \int d^3r e^{-i\vec{q}\cdot\vec{r}} e^{-r/a_0} = \sqrt{\pi a_0^3} \frac{8}{(1 + a_0^2 q^2)^2} \quad (8.85)$$

Combining these results we obtain, finally:

$$\begin{aligned} \frac{d\Gamma_0(\theta, \phi)}{d\Omega} &= \frac{16mV_0^2 a_0^2}{\pi \hbar^3} \frac{ka_0}{(1 + a_0^2 |\vec{k} - \vec{k}_0|^2)^4} \\ &= \frac{16mV_0^2 a_0^2}{\pi \hbar^3} \frac{ka_0}{(1 + a_0^2 (k^2 - 2kk_0 \cos \theta + k_0^2))^4} \end{aligned} \quad (8.86)$$

which is symmetric about the z -axis (independent of ϕ) and has a maximum along the z direction associated with the wavevector \vec{k}_0 that characterizes the perturbation (suggesting the absorption of momentum from the plane wave perturbation). Note that although we adopted the “box convention” for determining the density of states, corresponding factors in the normalization of the final plane wave state led to a cancellation of any terms involving the size L of the box. We are free at this point to take $L \rightarrow \infty$ without affecting the final answer.

8.3 Perturbations that Turn On

We now consider another class of problems, one in which the measurement question that is asked is slightly different. Consider a system subject to a time dependent perturbation

$$H(t) = H_0 + \hat{V}(t) \quad (8.87)$$

in which the perturbation begins to be applied to the system at some fixed instant of time (say $t = 0$), but takes a certain amount of time to develop. (The current has to build up in the external circuits, for example). To describe this situation, we write the perturbation in the form

$$\hat{V}(t) = V_0 \lambda(t) \quad (8.88)$$

where the function $\lambda(t)$ describes the smooth increase in the strength of the perturbation \hat{V} to its final value V_0 . The function $\lambda(t)$ is unspecified, but is assumed to have the general features

$$\lambda(t) = \begin{cases} 0 & \text{for } t < 0 \\ 1 & \text{for } t > T \end{cases} \quad (8.89)$$

where T is a measure of the time that it takes for the perturbation to build up to full strength. We note that except for the interval $T > t > 0$, while the Hamiltonian is actually changing, the system is described by time-independent Hamiltonia: H_0 initially, and $H_0 + V_0$ afterwards. During these initial and final intervals the evolution is readily described by the corresponding eigenvectors and eigenvalues of these two different operators. Borrowing from the notation we introduced previously, we denote by $|n^{(0)}\rangle$ and $\epsilon_n^{(0)}$ the eigenvectors and eigenvalues of H_0 and by $|n\rangle$ and ϵ_n the corresponding quantities for the final Hamiltonian $H = H_0 + V_0$. Then, by assumption,

$$\begin{aligned} H_0 |n^{(0)}\rangle &= \epsilon_n^{(0)} |n^{(0)}\rangle \\ (H_0 + V_0) |n\rangle &= \epsilon_n |n\rangle \end{aligned} \quad (8.90)$$

We then ask the following question. If the system is known to be in an eigenstate $|n^{(0)}\rangle$ of H_0 at $t = 0$, what is the amplitude for it to be in the eigenstate $|n'\rangle$ of the *final* Hamiltonian $H = H_0 + V_0$ after the perturbation has fully turned on? This is clearly a relevant question, since information about the admixture of final eigenstates allows us to predict the subsequent evolution for $t > T$. So the basic question is, what happens to the system as the perturbation is increasing to its final form? The general answer to this question is complicated, but becomes very simple in two limiting cases: (1) a perturbation that is applied infinitely fast, and (2) a perturbation that is applied infinitely slowly.

The first, referred to as a *sudden perturbation* occurs when the change in the Hamiltonian occurs much more rapidly than the system (either before or after the change) can respond. In this limit, the function $\lambda(t) = \theta(t)$ is essentially a Heaviside step function. The opposite limit, that in which the turn-on time T is much longer than typical evolution times of the system describes what is referred to as an *adiabatic perturbation*.

As a useful thought-experiment that provides a mental mnemonic for remembering what happens in these two cases, consider what happens when a marble is placed in the bottom (i.e., ground state) of a bowl, which is then raised slowly to some predetermined height. If the raised bowl is then suddenly lowered, the marble will be left hanging in air, in the “ground state” of the raised bowl, not the lowered one. It does not have time, under these circumstances to respond to the changing conditions (Hamiltonian) until long after the bowl is in the lowered position. When, on the other hand, the bowl is lowered very slowly, the marble stays in the “instantaneous ground state” of the bowl for each elevation, ultimately sitting in the bottom of the bowl in the final lowered position. These features also characterize the behavior of quantum mechanical systems.

8.3.1 Sudden Perturbations

In keeping with the thought experiment just described, it is possible to show quite generally that the state vector $|\psi(t)\rangle$ of a system subject to an instantaneous change in its Hamiltonian undergoes no change itself as a result of the instantaneous change in the H . In such a circumstance, the Schrödinger equation can be written (in the so-called sudden approximation) in the form

$$\begin{aligned} \left(i\hbar\frac{d}{dt} - H_0\right)|\psi(t)\rangle &= 0 & t < 0 \\ \left(i\hbar\frac{d}{dt} - H_0 - V_0\right)|\psi(t)\rangle &= 0 & t > 0 \end{aligned} \quad (8.91)$$

To understand what happens to the state vector during this change, we formally integrate across the discontinuity in $H(t)$ at $t = 0$, as follows:

$$d|\psi(t)\rangle = \frac{-i}{\hbar} \left[H_0|\psi(t)\rangle + \theta(t)\hat{V}_0|\psi(t)\rangle \right] dt \quad (8.92)$$

$$\int_{\psi_-}^{\psi_+} d|\psi(t)\rangle = \frac{-i}{\hbar} \int_{-\varepsilon}^{+\varepsilon} H_0|\psi(t)\rangle dt - \frac{i}{\hbar} \int_0^{\varepsilon} V_0|\psi(t)\rangle dt \quad (8.93)$$

Thus, we find that, for infinitesimal ε

$$|\psi_+\rangle - |\psi_-\rangle = -\frac{i}{\hbar}\varepsilon H_0|\psi_+\rangle + \frac{i}{\hbar}\varepsilon H_0|\psi_-\rangle - \frac{i}{\hbar}\varepsilon V_0|\psi_+\rangle \quad (8.94)$$

The right hand side is proportional to ε , so provided that the strength of \hat{V}_0 is finite,

$$\lim_{\varepsilon \rightarrow 0} |\psi_+\rangle - |\psi_-\rangle = 0. \quad (8.95)$$

Hence $|\psi(t)\rangle$ is continuous across any finite discontinuity in H . Thus in this limit, if the system is initially in an eigenstate $|n^{(0)}\rangle$ of H_0 , it will still be in that state immediately after the change in the Hamiltonian has occurred. The transition amplitude to find it, at that instant, in the eigenstate $|n'\rangle$ of $H_0 + \hat{V}_0$ is just the inner product between the eigenstates of these two different Hamiltonia, i.e.,

$$T_{n \rightarrow n'} = \langle n' | n^{(0)} \rangle \quad W_{n \rightarrow n'} = \left| \langle n' | n^{(0)} \rangle \right|^2 \quad (8.96)$$

As an interesting example of this class of problem, consider the beta decay of the tritium atom, which is an isotope of hydrogen with a nucleus consisting of 2 neutrons and 1 proton, so $Z = 1$. Suppose the single bound electron of this atom, which sees an electric potential identical to that of hydrogen, is initially in its ground state, when the tritium nucleus to which it is bound undergoes beta decay, a process in which the nucleus ejects an electron with high kinetic energy (~ 17 KeV), leaving behind a Helium nucleus with 2 protons and a neutron. As a result of the quick ejection of the “nuclear” electron, the bound atomic electron sees the potential in which its moving change very quickly from

$$V_i = -\frac{e^2}{r} \quad (8.97)$$

to

$$V_f = -\frac{2e^2}{r}. \quad (8.98)$$

Thus, immediately after the beta decay the electron is in the ground state of Hydrogen,

$$\psi_{1,s}(\vec{r}, Z = 1) = \langle \vec{r} | \psi \rangle = \frac{1}{\sqrt{\pi a_0^3}} \exp(-r/a_0) \quad (8.99)$$

but is moving in a potential corresponding to singly ionized Helium (He^+). It is, therefore, in a linear combination of Helium ion ground and excited eigenstates. What is the probability amplitude that an energy measurement will find the electron in, say, the $\psi_{2,s}$ state of the Helium ion? It is just the inner product between the ψ_{1s} ground state of Hydrogen (with $Z = 1$) and the corresponding ψ_{2s} state (with $Z = 2$) for the He ion. For a hydrogenic atom with $Z = 2$,

$$\psi_{2s} = \psi_{2,0,0} = \frac{1}{\sqrt{\pi a_0^3}} \left(1 - \frac{r}{a_0}\right) e^{-r/a_0} \quad (8.100)$$

so the relevant transition amplitude is

$$\begin{aligned} T_{1s \rightarrow 2s} &= \int d^3r \psi_{2s}^*(2, r) \psi_{1s}(1, r) = \frac{4}{a_0^3} \int_0^\infty dr r^2 \left(1 - \frac{r}{a_0}\right) e^{-2r/a_0} = -\frac{1}{2}, \\ W_{1s \rightarrow 2s} &= \frac{1}{4} \end{aligned} \quad (8.101)$$

There is, therefore, a 25% chance of it ending up in this state. Such transitions can be detected when the electron emits a photon and decays back to the ground state of the He ion. Obviously the emission spectrum for this process can be calculated by finding the corresponding transition probabilities for the remaining excited states of the He^+ ion.

8.3.2 The Adiabatic Theorem

Perturbations that reach their full strength very slowly obey the so-called *adiabatic theorem*: if the system is initially in an eigenstate $|n^{(0)}\rangle$ of H_0 before the perturbation starts to change, then provided the change in H occurs slowly enough, it will adiabatically follow the change in the Hamiltonian, staying in an instantaneous eigenstate of $H(t)$ while the change is taking place. Afterwards, therefore, it will be found in the corresponding eigenstate $|n\rangle$ of the final Hamiltonian $H = H_0 + V_0$.

To see this we present a “perturbative proof” of the adiabatic theorem, by focusing on an interval of time over which the Hamiltonian changes by a very small amount. Now, by assumption, the Hamiltonian $H(t)$ of the system is evolving very slowly in time and may ultimately change by a great amount. Suppose, however, that there exists an instant during this evolution when the system happens to be in an instantaneous eigenstate $|n\rangle$ of $H(t)$. Let us redefine our time scale and denote this instant of time as $t = 0$, and set $H_0 = H(0)$. At some time T later, the Hamiltonian will have evolved into a new operator $H(T) = H_0 + \hat{V}$, where the change in H , represented by the operator $\hat{V} = H(T) - H_0$, is assumed small, in the perturbative sense, compared to H_0 . We are interested in exploring how the evolution of the system during this time interval depends upon the total time T for this change in the Hamiltonian to take place. As already discussed, we assume that the Hamiltonian varies in the intervening time interval $T > t > 0$ in such a way that $V(t) = H(t) - H_0 = \lambda(t)\hat{V}$, where the function $\lambda(t)$ starts at $t = 0$ with the value $\lambda(0) = 0$ and increases monotonically to the final value $\lambda = 1$ when $t = T$. To allow for a parameterization of the speed with which the change in H occurs, we assume that the function λ can be reexpressed in the form $\lambda = \lambda(t/T) = \lambda(s)$, with the properties that $\lambda(0) = 0$ and $\lambda(1) = 1$. This allows us to smoothly decrease the rate at which the change in H is being made simply by increasing the time T over which the change occurs. For convenience, we also make the assumption that $\lambda(s)$ is a monotonically increasing

function of $s = t/T$ for s between 0 and 1. Under these circumstances, for sufficiently small perturbations \hat{V} , the state at the end of this interval of time will be given to an excellent approximation by the results of first order time-dependent perturbation theory:

$$U(T, 0)|n^{(0)}\rangle = \sum_m \psi_m(T)|m^{(0)}\rangle \quad (8.102)$$

with

$$\begin{aligned} \psi_n(T) &= e^{-i\omega_n T} \\ \psi_m(T) &= -\frac{i}{\hbar} e^{-i\omega_m T} \int_0^T dt V_{m,n}(t) e^{i\omega_{mn} t} \\ &= -\frac{iV_{mn}}{\hbar} e^{-i\omega_m T} \int_0^T dt \lambda(t/T) e^{i\omega_{mn} t} \quad m \neq n. \end{aligned} \quad (8.103)$$

Performing an integration by parts, and using the limiting values of the function $\lambda(t/T)$ over this interval, leads then to the result

$$\psi_m(t) = -\frac{V_{mn} e^{-i\omega_m T} e^{i\omega_{mn} T}}{\omega_{mn}} + \frac{V_{mn} e^{-i\omega_m T} e^{i\omega_{mn} T}}{\omega_{mn}} \int_0^T dt \frac{d\lambda(t/T)}{dt} e^{i\omega_{mn} t}. \quad (8.104)$$

Now in the limit that the time T over which this change takes place becomes very large, the second integral becomes as small as we like. This follows from the fact that

$$\frac{d\lambda(t/T)}{dt} = \frac{1}{T} \lambda'(t/T) = \frac{d\lambda(s)}{ds} \Big|_{s=t/T}. \quad (8.105)$$

Thus the integral of interest is bounded in magnitude by the relation

$$\begin{aligned} \left| \int_0^T dt \frac{d\lambda(t/T)}{dt} e^{i\omega_{mn} t} \right| &\leq \frac{1}{T} \int_0^T dt |\lambda'(t/T) e^{i\omega_{mn} t}| = \frac{1}{T} \int_0^T dt \lambda'(t/T) \\ &= \frac{\lambda(1) - \lambda(0)}{T} = \frac{1}{T}. \end{aligned} \quad (8.106)$$

where in evaluating the last integral we have used the assumed monotonicity of λ . Hence the second term in the previous integration by parts is of order $1/T$ and becomes negligible relative to the first as $T \rightarrow \infty$. In this limit, then, the first term gives for $m \neq n$ the result

$$\psi_m(T) = -\frac{V_{mn} e^{-i\omega_m T} e^{i\omega_{mn} T}}{\hbar\omega_{mn}} = -\frac{V_{mn} e^{-i\omega_n T}}{\varepsilon_m^{(0)} - \varepsilon_n^{(0)}}, \quad (8.107)$$

where we have used the definition of ω_{mn} in terms of the corresponding eigenvalues of H_0 . Thus, to this order we can write

$$\begin{aligned} |\psi(t)\rangle &= e^{-\omega_n t} |n^{(0)}\rangle + e^{-i\omega_n t} \sum_{m \neq n} \frac{V_{mn}}{\varepsilon_m^{(0)} - \varepsilon_n^{(0)}} |m^{(0)}\rangle \\ &= e^{-\omega_n t} |n\rangle \end{aligned} \quad (8.108)$$

where

$$|n\rangle = |n^{(0)}\rangle + \sum_{m \neq n} \frac{V_{mn}}{\varepsilon_m^{(0)} - \varepsilon_n^{(0)}} |m^{(0)}\rangle \quad (8.109)$$

is the perturbative result for the exact eigenstate of $H(T) = H_0 + \hat{V}$ expressed as an expansion in eigenstates of $H_0 = H(0)$. Thus, if the system begins the time interval in

an eigenstate $|n^{(0)}\rangle$ of $H(0)$, it ends in an eigenstate $|n\rangle$ of $H(T)$. We can now repeat the process, presumably, by redefining the time such that $t = T$ corresponds to a new time variable $t' = 0$, redefine H_0 as $H(T) = H(t' = 0)$, and proceed in the same way as above. In this way, after many such (long) time intervals, the system has remained in the corresponding eigenstate of the evolving Hamiltonian, which can ultimately change by a very great amount. Provided that the change occurs sufficiently slowly, however, the state of the system will adiabatically “follow” the slowly-evolving Hamiltonian. Thus, the amplitude to find the system in an eigenstate of the final Hamiltonian is unity, provided it started in the corresponding eigenstate of the initial Hamiltonian.

If the change that occurs in the Hamiltonian is not infinitely slow, however, there will be transitions induced to other eigenstates of $H(T)$. In the case of a pair of energy levels that are made to cross as a result of a time dependent perturbation it is possible to determine the probability of transitions being induced between different corresponding levels. The resulting analysis of such “Landau-Zener” transitions is presented in an appendix. The details are a bit complicated and rely on properties of the parabolic cylinder functions. The end result, however, is the surprisingly simple expression

$$W = \exp\left(-\frac{\pi V^2}{\hbar |d\varepsilon/dt|}\right) \quad (8.110)$$

for the transition probability between a pair of levels whose time-dependent energies cross at a rate $d\varepsilon/dt$ and which are connected by a constant matrix element V . Note that as the time rate of change of the perturbation goes to zero, the transition probability becomes exponentially small, and can, consistent with the adiabatic theorem, be neglected provided

$$d\varepsilon/dt \ll \pi V^2/\hbar. \quad (8.111)$$

8.4 Appendix: Landau-Zener Transitions

Consider a pair of energy levels connected by a constant matrix element V . If the (diagonal) energies of the original states remain constant, then the probability amplitude to be found in either one will oscillate in time with a frequency proportional to V and with an amplitude that depends upon the magnitude of the energy difference between them. For widely separated levels very little amplitude is ever transferred from one state to the other. Even when the levels are degenerate, the transfer is complete but temporary, since the amplitude repeatedly oscillates entirely back to the original state. Consider, however, a time-dependent perturbation that causes two widely separated levels connected by a constant matrix element to temporarily become close, or even degenerate in energy, and then to separate. In this situation an irreversible transition can occur as a result of the strong transfer that takes place during the limited time that the levels are nearly degenerate, since some fraction of the amplitude will generally get “stranded” in each state as the levels become widely separated again in energy. Processes of this type are referred to as Landau-Zener transitions since they were originally studied independently by those two authors in the context of electronic transitions in molecular systems during collisions. The basic idea has a wider applicability and has more recently been applied to understand optically induced transitions between Stark-split states of atomic systems within the so-called dressed atom picture of Cohen-Tanoudji, et al.

To understand the essence of the Landau-Zener transition we consider two states $|\phi_1\rangle$ and $|\phi_2\rangle$, subject to a time-dependent Hamiltonian $H(t)$ for which

$$\begin{aligned} H(t)|\phi_1\rangle &= \hbar\omega_1(t)|\phi_1\rangle + \hbar v|\phi_2\rangle \\ H(t)|\phi_2\rangle &= \hbar\omega_2(t)|\phi_2\rangle + \hbar v|\phi_1\rangle \end{aligned}$$

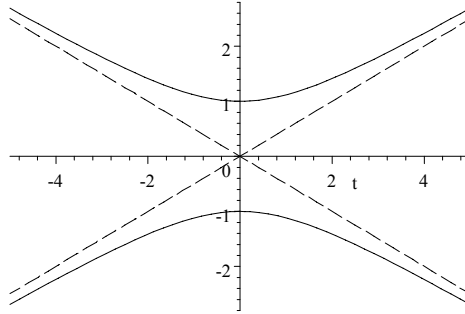
where, for simplicity, $\omega_1(t)$ and $\omega_2(t)$ are taken to be linear functions of time such that $\omega_2(t) = -\omega_1(t) = \alpha t/2$, with $\alpha > 0$. Thus, ω_2 is negative for negative times and positive for positive times, while ω_1 has the opposite behavior. At very large negative times the levels are widely separated with a positive energy splitting

$$\omega = \omega_1 - \omega_2 = -\alpha t$$

indicating that $\omega_1 > \omega_2$ for $t < 0$. These “bare” energy levels come together and cross at $t = 0$, with ω_2 becoming larger than ω_1 for $t > 0$. The exact instantaneous eigenenergies and eigenstates $|\psi_+\rangle$ and $|\psi_-\rangle$ are easily determined by diagonalizing the 2×2 matrix associated with $H(t)$; the two roots to the secular equation

$$E_{\pm}(t) = \pm \hbar \sqrt{v^2 + \frac{1}{4}\alpha^2 t^2}$$

are indicated schematically below along with the bare energies.



Clearly, at large negative times ω_2 corresponds to the lower branch E_- and ω_1 to the upper branch E_+ . The situation becomes reversed at large positive times, where ω_2 corresponds to E_+ and ω_1 to E_- . Thus, up to a phase factor,

$$\lim_{t \rightarrow \infty} \psi_+(t) = \lim_{t \rightarrow -\infty} \psi_-(t) = \phi_2 \qquad \lim_{t \rightarrow \infty} \psi_-(t) = \lim_{t \rightarrow -\infty} \psi_+(t) = \phi_1$$

In the neighborhood of $t = 0$, the exact eigenstates are nearly equal symmetric and antisymmetric combinations of $|\phi_1\rangle$ and $|\phi_2\rangle$, and the two branches associated with the exact eigenenergies exhibit the classic “avoided crossing” behavior, never coming any closer together in energy than $2V = 2\hbar v$. Suppose that initially, as $t \rightarrow -\infty$, the system is in the ground state $|\phi_2\rangle = |\psi_-(-\infty)\rangle$, i.e., on the lower branch $E_-(t)$. Then, according to the adiabatic theorem, provided $H(t)$ is varied slowly enough ($\alpha \ll 1$), the system will remain on this lower branch at each instant as the system adiabatically evolves. At large positive times, therefore, the system will (up to a phase) be in the state $|\phi_1\rangle = |\psi_-(+\infty)\rangle$ with unit probability. On the other hand, transitions between the upper and lower branches may occur if the variation is not sufficiently slow.

To analyze this process, we consider the following expansion

$$|\psi(t)\rangle = C_1(t)e^{-i\Phi_1(t)}|\phi_1\rangle + C_2(t)e^{-i\Phi_2(t)}|\phi_2\rangle$$

for the state of the system, where

$$\Phi_i(t) = \int_0^t \omega_i(t') dt' \qquad d\Phi_i/dt = \omega_i(t).$$

Substitution into the Schrödinger equation

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H(t) |\psi(t)\rangle$$

yields the following set of first order differential equations

$$i \frac{dC_1}{dt} = v e^{i \int_0^t \omega dt'} C_2 \quad i \frac{dC_2}{dt} = v e^{-i \int_0^t \omega dt'} C_1.$$

for the expansion coefficients. We seek solutions to these equations corresponding to the boundary conditions

$$|C_1(-\infty)| = 0 \quad |C_2(-\infty)| = 1,$$

in which the system is initially in an eigenstate associated with the lower branch E_- of the energy spectrum, and we are interested in the probability that at large positive times, well after the levels have separated and are no longer strongly-interacting, the system has made a transition from the lower branch E_- to the upper branch E_+ . In this regime E_+ corresponds to the state $|\phi_2\rangle$. Thus, the transition probability arising from the nonadiabaticity of the perturbation is given by

$$P = |C_2(+\infty)|^2 = 1 - |C_1(+\infty)|^2.$$

To proceed, we take another derivative and substitute back in to obtain the following pair of second order differential equations

$$\frac{d^2 C_1}{dt^2} - i\omega \frac{dC_1}{dt} + v^2 C_1 = 0 \quad \frac{d^2 C_2}{dt^2} + i\omega \frac{dC_2}{dt} + v^2 C_2 = 0,$$

The substitutions

$$C_1 = U_1 \exp\left(\frac{i}{2} \int_0^t \omega dt'\right) \quad C_2 = U_2 \exp\left(-\frac{i}{2} \int_0^t \omega dt'\right)$$

along with the relation $d\omega/dt = -\alpha$ reduce these to

$$\frac{d^2 U_1}{dt^2} + \left(v^2 - \frac{i\alpha}{2} + \frac{\alpha^2 t^2}{4}\right) U_1 = 0 \quad \frac{d^2 U_2}{dt^2} + \left(v^2 + \frac{i\alpha}{2} + \frac{\alpha^2 t^2}{4}\right) U_2 = 0.$$

A final pair of substitutions

$$z = \alpha^{1/2} e^{-i\pi/4} t \quad n = iv^2/\alpha = i\gamma$$

where $\gamma = v^2/\alpha$ is positive and real, put these into the standard differential equations

$$\begin{aligned} \frac{d^2 U_1}{dz^2} - \left(\frac{1}{4}z^2 - n - \frac{1}{2}\right) U_1 &= \frac{d^2 U_1}{dz^2} - \left(\frac{1}{4}z^2 + a_1\right) U_1 = 0 \\ \frac{d^2 U_2}{dz^2} - \left(\frac{1}{4}z^2 - n + \frac{1}{2}\right) U_2 &= \frac{d^2 U_2}{dz^2} - \left(\frac{z^2}{4} + a_2\right) U_2 = 0 \end{aligned}$$

obeyed by the parabolic cylinder functions $U(a, z)$, where here $a_1 = -n - \frac{1}{2}$ and $a_2 = -n + \frac{1}{2}$.

The solution to the first of these equations having the right properties as $t \rightarrow \pm\infty$ is the parabolic cylinder function

$$U_1(z) = AU(-a_1, -iz) = AU(a, -iz),$$

where $a = n + \frac{1}{2}$ and the constant A must be determined from the initial conditions and the asymptotic properties of the functions $U(a, x)$. As $t \rightarrow -\infty$ the argument of the function can be written $-iz \rightarrow ie^{-i\pi/4} |\alpha^{1/2} t| = e^{i\pi/4} R$, with $R \rightarrow \infty$ real and positive, along which path*

$$U_1 = AU(a, -iz) \sim AU(a, Re^{i\pi/4}) \sim Ae^{-\frac{1}{4}iR^2} R^{-n-1} e^{-i\pi(n+1)/4}.$$

This clearly goes to zero as $R \rightarrow \infty$ as $1/R$ (note that $R^{-n} = e^{-i\gamma \ln R}$ oscillates with unit magnitude as R increases because n is strictly imaginary). Thus this solution automatically satisfies the initial condition $|C_1(-\infty)| = |U_1(-\infty)| = 0$. To determine the value of A we use the other initial condition

$$1 = |C_2(-\infty)| = \frac{1}{v} \lim_{t \rightarrow -\infty} \left| \frac{dC_1}{dt} \right|$$

where we have used the original differential equation to express C_2 in terms of the derivative of C_1 . Now using the relation between C_1 and U_1 the boundary condition for U_1 becomes

$$1 = \lim_{t \rightarrow -\infty} v^{-1} \left| -\frac{i\omega}{2} U_1 + \frac{dU_1}{dt} \right|$$

It turns out that as $t \rightarrow -\infty$ the first term in the brackets has precisely the same asymptotic behavior

$$\begin{aligned} -\frac{i\omega}{2} U_2 &= -\frac{i\alpha t}{2} U_1 \sim -\frac{1}{2} i A \alpha^{1/2} R e^{-\frac{1}{4}iR^2} R^{-n-1} e^{-i\pi(n+1)/4} \\ &\sim -\frac{iA}{2} \alpha^{1/2} e^{-\frac{1}{4}iR^2} R^{-n} e^{-i\pi(n+1)/4}, \end{aligned}$$

as the second term

$$\begin{aligned} \frac{dU_1}{dt} &= A\alpha^{1/2} \frac{dU(a, Re^{i\pi/4})}{dR} \sim A\alpha^{1/2} \frac{d}{dR} \left[e^{-\frac{1}{4}iR^2} R^{-n-1} e^{i\pi(n+1)/4} \right] \\ &\sim -\frac{iA}{2} \alpha^{1/2} e^{-\frac{1}{4}iR^2} R^{-n} e^{-i\pi(n+1)/4}. \end{aligned}$$

Thus the boundary condition becomes

$$1 = \lim_{R \rightarrow \infty} v^{-1} \left| -iA\alpha^{1/2} e^{-\frac{1}{4}iR^2} R^{-n} e^{-i\pi(n+1)/4} \right| = |A| \gamma^{-1/2} e^{\pi\gamma/4},$$

from which we deduce that

$$|A| = \gamma^{1/2} e^{-\pi\gamma/4}.$$

At large positive times the argument of the parabolic cylinder function can be written $-iz \rightarrow -ie^{-i\pi/4} |\alpha^{1/2} t| = Re^{-i3\pi/4}$. To determine the asymptotic properties in this situation we use the identity†

$$\sqrt{2\pi} U\left(-a, Re^{-i\pi/4}\right) = \Gamma\left(\frac{1}{2} + a\right) \left\{ e^{-i\frac{\pi}{2}(-a+\frac{1}{2})} U\left(a, Re^{i\pi/4}\right) + e^{i\frac{\pi}{2}(-a+\frac{1}{2})} U\left(a, Re^{-i3\pi/4}\right) \right\}$$

*From Abramowitz and Stegun, p.689, Eq. 19.8.1 we have for $|x| \gg |a|$ when $|\arg x| < \pi/2$, that

$$U(a, x) \sim e^{-x^2/4} x^{-a-1/2}$$

†Here we use, with $x = Re^{-i\pi/4}$ the expression from Abramowitz and Stegun, p. 687, Eq. 19.4.6, which gives

$$\sqrt{2\pi} U(a, \pm x) = \Gamma\left(\frac{1}{2} - a\right) \left\{ e^{-i\pi(\frac{1}{2}a+\frac{1}{4})} U(-a, \pm ix) + e^{i\pi(\frac{1}{2}a+\frac{1}{4})} U(-a, \mp ix) \right\}$$

which implies that as $t \rightarrow +\infty$

$$\begin{aligned} U_1 &= AU(a, Re^{-i3\pi/4}) = A \left[e^{i\pi(n+1)} U(a, Re^{i\pi/4}) + \frac{\sqrt{2\pi}}{\Gamma(n+1)} e^{i\pi n/2} U(-a, Re^{-i\pi/4}) \right] \\ &\sim A \left[e^{i3\pi(n+1)/4} e^{-\frac{1}{4}iR^2} R^{-n-1} + \frac{\sqrt{2\pi}}{\Gamma(n+1)} e^{i\pi n/2} e^{\frac{1}{4}iR^2} R^n e^{-i\pi n/4} \right] \sim \frac{A\sqrt{2\pi}}{\Gamma(n+1)} e^{i\pi n/2} e^{\frac{1}{4}iR^2} R^n e^{-i\pi n/4} \end{aligned}$$

and so

$$|U_1(+\infty)| = \frac{\sqrt{2\pi\gamma}}{\Gamma(n+1)} e^{-\pi\gamma/2}.$$

The square of this gives the amplitude for the system to remain on the lower branch E_- , i.e.,

$$\begin{aligned} |C_1(\infty)|^2 &= \lim_{R \rightarrow +\infty} |U_1(Re^{-i\pi/4})|^2 = \frac{2\pi\gamma}{\Gamma(1+i\gamma)\Gamma(1-i\gamma)} e^{-\pi\gamma} \\ &= 2e^{-\pi\gamma} \sinh \pi\gamma = 1 - e^{-\pi\gamma} \end{aligned}$$

and so the corresponding transition probability to the upper branch is given by the Landau-Zener formula

$$\begin{aligned} P &= 1 - |C_1(\infty)|^2 \\ &= e^{-\pi\gamma} = \exp(-\pi V^2/\hbar^2\alpha) = \exp\left(-\frac{\pi V^2}{\hbar^2 |d\omega/dt|}\right). \end{aligned}$$