Phys 852, Quantum mechanics II, Spring 2009

Time-Dependent Perturbation Theory

Prof. Michael G. Moore, Michigan State University

1 The central problem in time-dependent perturbation theory:

In time-independent perturbation theory, the object was to find the new eigenvalues and eigenstates when a system whose states are known is 'perturbed' by adding an additional term to the Hamiltonian. The main trick was to multiply the perturbation operator by λ, and then expand both the states and eigenvalues in a power series in λ. Inserting these two expansions into the energy eigenvalue equation and equating terms of equal powers of λ led to a systematic way to build up an approximate solution. At the end λ can be set to unity to match the solution to the original Hamiltonian.

In time-dependent perturbation theory the main goal is to determine the time-evolution of a perturbed quantum system, with particular emphasis on calculating transition probabilities and modeling the irreversible decay of probability from a small quantum system coupled to a very large quantum system.

Formally, we want to find the time evolution of a state governed by the Schrödinger Equation,

$$\frac{d}{dt}|\psi(t)\rangle = -\frac{i}{\hbar}\left(H_0 + V(t)\right)|\psi(t)\rangle, \tag{1}$$

where H_0 is the 'bare' Hamiltonian, whose eigenstates and eigenvalues are known, and $V(t)$ is some perturbation. Experimentally, important information can be obtained by observing how a system responds when we 'wiggle' it or 'kick' it, or otherwise perturb it in a time-dependent way. While $V(t)$ is thus explicitly taken as time-dependent, time-dependent perturbation theory is equally suited to the case where V is constant in time.

In order to keep track of perturbation 'order', it is customary to introduce the perturbation parameter, λ, and start from the Hamiltonian

$$H = H_0 + \lambda V(t), \tag{2}$$

and then set $\lambda = 1$ at the end of the calculation.

Generally, we will assume that the system starts in one of the unperturbed eigenstates, which we will refer to as $|m\rangle$. But the perturbation approach applies equally well to an arbitrary initial state $|\psi(0)\rangle$, i.e. s a superposition of bare eigenstates. The goal is to find $|\psi(t)\rangle$, the state at some later time t. In principle, one can simply start by inserting a perturbation expansion for $|\psi(t)\rangle$ into Eq. (1), and start turning the crank. However, we can make things much easier on ourselves by (a) computing the perturbed propagator, which can then be used to propagate any initial state; and (b) switching to the interaction picture, where the calculation are much cleaner. Thus we will first briefly review the tranformation between the Schrödinger and Interaction pictures.

2 Theory of Hilbert-space frame transformations

In Schrödinger's formulation of quantum mechanics, a quantum system is described by a state vector, $|\psi(t)_S\rangle$, whose time evolution is governed by

$$\frac{d}{dt}|\psi(t)_S\rangle = -\frac{i}{\hbar}H_S|\psi(t)_S\rangle, \tag{3}$$

where H_S is the 'Hamiltonian' operator, and the subscript 'S' indicates that this is the Schrödinger picture of Quantum Mechanics. Observables in the Scrhödinger picture correspond to stationary operators, whose average values are given by

$$\langle O\rangle = \langle\psi(t)|O_S|\psi(r)\rangle, \tag{4}$$

where O_S represents any observable quantity.

The state at time t must be related to the state at time $t = 0$ by a unitary transformation, thus we can define the 'Schrödinger picture propagator' via

$$|\psi_S(t)\rangle = U_S(t)|\psi_S(0)\rangle. \tag{5}$$

Substituting this into (3) then gives

$$\frac{d}{dt}U_S(t)|\psi_S(0)\rangle = -\frac{i}{\hbar}H_S U_S(t)|\psi_S(0)\rangle. \tag{6}$$

As this equation must be valid for any initial state, it follows that $U_S(t)$ is governed by the equation

$$\frac{d}{dt}U_S(t) = -\frac{i}{\hbar}H_S U_S(t), \tag{7}$$

subject to the initial condition $U_S(0) = I$.

In terms of the propagator, expectation values of observables are given by

$$\langle O\rangle = \langle\psi(0)|U_S^\dagger(t)O_S U_S(t)|\psi(0)\rangle. \tag{8}$$

The then begs the question, why do we associate the propagator with the state-vector, and not with the observables. After all, in classical physics, it is the observables that evolve in time, and there is no concept of a 'state' abstracted from the values of particular observables. Clearly, developing the concept of a quantum state-vector is a major advancement in quantum theory, precisely because it decouples the 'state' of the system from the values of observables, such that once the 'state' is known, the value of any observable, including its quantum uncertainties and correlations, can be computed directly from the 'state'.

2.1 The Heisenberg picture

Never-the-less, one can ask what Quantum Mechanics might look like, if we attached the propagator to the observable instead of the state vector. In fact, this is exactly how Heisenberg, working independently of Schrödinger, formulated his own version of Quantum theory. Operators in the 'Heisenberg picture' are related to their Schrödinger picture counterparts via

$$O_H(t) = U_S^\dagger(t)O_S U_S(t), \tag{9}$$

which leads to the 'Heisenberg equation of motion',

$$\begin{aligned}\frac{d}{dt}O_H &= \dot{U}_S^\dagger O_S U_S + U_S^\dagger O_S \dot{U}_S \\ &= \frac{i}{\hbar}U_S^\dagger H_S O_S U_S - \frac{i}{\hbar}U_S^\dagger O_S H_S U_S \\ &= \frac{i}{\hbar}U_S^\dagger H_S U_S^\dagger U_S O_S U_S - \frac{i}{\hbar}U_S^\dagger O_S U_S^\dagger U_S H_S U_S \\ &= \frac{i}{\hbar}[H_H, O_H]. \end{aligned} \tag{10}$$

If we take

$$[A_S, B_S] = M_S, \tag{11}$$

i.e. the operator M_S is generated by the commutator of A with B in the Schrödinger picture, then it follows that

$$[A_H, B_H] = M_H. \tag{12}$$

The proof is as follows,

$$\begin{aligned}[A_H, B_H] &= A_H B_H - B_H A_H \\ &= U_S^\dagger A_S U_S U_S^\dagger B U_S - U_S^\dagger B_S U_S U_S^\dagger A U_S \\ &= U_S^\dagger A_S B_S U_S - U_S^\dagger B_S A_S U_S \\ &= U_S^\dagger [A_S, B_S] U_S \\ &= U_S^\dagger M_S U_S \\ &= M_H. \end{aligned} \tag{13}$$

This means that the algebraic structure of the operators is invariant when transforming from one picture to the other, which allows to drop the subscripts and write

$$[A, B] = M, \tag{14}$$

which is valid in all frames. For example from $[X, P] = i\hbar$, it follows that $[X_S, P_S] = i\hbar$ and also $[X_H, P_H] = i\hbar$.

In contrast to the Schrödinger picture, the state-vector in the Heisenberg picture is time-independent. It is related to the time-dependent state-vector in the Schrödinger picture by

$$|\psi_H\rangle = |\psi_S(0)\rangle, \tag{15}$$

and expectation values are taken via

$$\langle O \rangle = \langle \psi_H | O_H(t) | \psi_H \rangle \tag{16}$$

That both theories give identical predictions is established by showing that both theories give identical results for expectation values of any and all operators, i.e.

$$\langle \psi_H | O_H(t) | \psi_H \rangle = \langle \psi_S(0) | U_S^\dagger(t) O_S U_S(t) | \psi_S(0) \rangle = \langle \psi_S(t) | O_S | \psi_S(t) \rangle. \tag{17}$$

2.2 Generalized Hilbert-space rotating-frame transformations

This transformation is a special case of a more general class of time-dependent unitary transformations that lead to a continuum of different 'pictures' or 'rotating frames', as they are commonly called, all of

which make identical physical predictions. The transformation from frame A to frame B is accomplished by transforming the state vector according to

$$|\psi_A(t)\rangle \rightarrow |\psi_B(t)\rangle = U_{BA}(t)|\psi_A(t)\rangle, \tag{18}$$

while at the same time transforming all operators according to

$$O_A(t) \rightarrow O_B(t) = U_{BA}(t)O_A(t)U_{AB}(t), \tag{19}$$

where $U_{BA}(t)$ is a unitary operator generated by a time-independent Hermitian operator, G, via

$$U_{BA}(t) = e^{iGt/\hbar}. \tag{20}$$

From this definition, we can see that the time-derivative of U_{BA} is

$$\dot{U}_{BA} = \frac{i}{\hbar}GU_{BA} = \frac{i}{\hbar}U_{BA}G. \tag{21}$$

The inverse transformation, U_{AB}, is given by

$$U_{AB}(t) = U_{BA}^{\dagger}(t) = e^{-iGt/\hbar}. \tag{22}$$

With these definitions, it follows that

$$U_{AB}(t)U_{BA}(t) = I, \tag{23}$$

which guarantees the invariance of observations,

$$\langle O\rangle_B = \langle\psi_B|O_B|\psi_B\rangle = \langle\psi_A|U_{AB}\,U_{BA}O_AU_{AB}\,U_{BA}|\psi_A\rangle = \langle\psi_A|O_A|\psi_A\rangle = \langle O\rangle_A. \tag{24}$$

Let us assume that the equation of motion for the state-vector in frame A is

$$\frac{d}{dt}|\psi_A\rangle = -\frac{i}{\hbar}H_{\psi,A}|\psi_A\rangle, \tag{25}$$

and that the equation of motion for the operators is

$$\frac{d}{dt}O_A = \frac{i}{\hbar}[H_{O,A}, O_A]. \tag{26}$$

Likewise, in frame B, the equations of motion are

$$\frac{d}{dt}|\psi_B\rangle = -\frac{i}{\hbar}H_{\psi,B}|\psi_B\rangle, \tag{27}$$

and

$$\frac{d}{dt}O_B = \frac{i}{\hbar}[H_{O,B}, O_B]. \tag{28}$$

The relationships between H_ψ and H_O in the two frames are readily derived by direct differentiation, which gives

$$\begin{aligned}\frac{d}{dt}|\psi_B\rangle &= \frac{d}{dt}U_{BA}|\psi_A\rangle \\ &= -\frac{i}{\hbar}\left(U_{BA}H_{\psi,A}U_{AB} - G\right)U_{BA}|\psi_A\rangle,\end{aligned} \tag{29}$$

from which we see that

$$H_{\psi,B} = U_{BA}H_{\psi,A}U_{AB} - G. \tag{30}$$

Likewise, diffenentiating O_B gives

$$\begin{aligned}\frac{d}{dt}O_B &= \frac{d}{dt}U_{BA}O_AU_{AB} \\ &= \frac{i}{\hbar}[U_{BA}H_{O,A}U_{AB}+G, O_B],\end{aligned} \tag{31}$$

which tells us that

$$H_{O,B} = U_{BA}H_{O,A}U_{AB} + G. \tag{32}$$

We note that the quantity $H = H_\psi + H_O$ is invariant, i.e.

$$H_{\psi,B} + H_{O,B} = H_{\psi,A} + H_{O,A}. \tag{33}$$

Which shows that the different reference frames correspond to different ways of dividing the Hamiltonian into two parts, and associating one part with the state, and the other with the operators.

We can define the time-propagator, $U_A(t)$, in frame A via

$$|\psi_A(t)\rangle = U_A(t)|\psi_A(0)\rangle, \tag{34}$$

and likewise, for frame B,

$$|\psi_B(t)\rangle = U_B(t)|\psi_B(0)\rangle. \tag{35}$$

To find the relation between the two time-propagators, we can start from Eq. (18), and use (34) to replace $|\psi_A(t)\rangle$, giving

$$|\psi_B(t)\rangle = U_{BA}(t)U_A(t)|\psi_A(0)\rangle. \tag{36}$$

At time $t = 0$, we have $U_{BA}(0) = U_{AB}(0) = I$, which means that the states and operators in both pictures are the same. Thus, $|\psi_A(0)\rangle = |\psi_B(0)\rangle$, which together with (35) yields

$$U_B(t)|\psi_B(0)\rangle = U_{BA}(t)U_A(t)|\psi_B(0)\rangle, \tag{37}$$

from which we see that

$$U_B(t) = U_{BA}(t)U_A(t). \tag{38}$$

We can see that neither H_ψ, H_O, nor the time-propagator transform as a normal operator, that is to say by Eq. (19). This is because the transformation is time-dependent, and these operators are defined solely by their operation in a given picture.

In this notation, the Schrödinger picture is defined by

$$H_{\psi,S} = H \tag{39}$$

and

$$H_{O,S} = 0, \tag{40}$$

with the Heisenberg picture corresponding to the opposite extreme

$$H_{\psi,H} = 0, \tag{41}$$

and

$$H_{O,H} = H. \tag{42}$$

The frame transformation $S \to H$ is generated by $G = H$, with the inverse transformation ($H \to S$) generated by $G = -H$.

2.3 The Interaction Picture

In perturbation theory, we divide the Hamiltonian into two parts via

$$H_S = H_0 + V, \tag{43}$$

where H_0 is the 'bare Hamiltonian', and V is the perturbation. This division leads to another common frame called the 'Interaction picture'. The transformation $S \to I$ is generated by $G = H_0$, giving

$$\begin{aligned} H_{\psi,I} &= U_{IS} H_{\psi,S} U_{SI} - G \\ &= U_{IS} H_0 U_{SI} + U_{IS} V U_{SI} - H_0 \\ &= U_{IS} V U_{SI} \\ &= V_I, \end{aligned} \tag{44}$$

and

$$\begin{aligned} H_{O,I} &= U_{IS} H_{O,S} U_{SI} + H_0 \\ &= H_0 \end{aligned} \tag{45}$$

so that the equations of motion are,

$$\frac{d}{dt}|\psi_I(t)\rangle = -\frac{i}{\hbar} V_I(t) |\psi_I(t)\rangle, \tag{46}$$

and

$$\frac{d}{dt} O_I(t) = \frac{i}{\hbar}[H_0, O_I(t)] \tag{47}$$

In terms of H_0, we see that

$$V_I(t) = e^{iH_0 t/\hbar} V e^{-iH_0 t/\hbar}, \tag{48}$$

where we can replace V with $V(t)$ in the case were the perturbation operator has explicit time-dependence in the Schrödinger picture. Commonly, one does not solve Eq. (47) to find the interaction-picture operators, but rather computes them directly from

$$O_I(t) = e^{iH_0 t/\hbar} O_S e^{-iH_0 t/\hbar}, \tag{49}$$

by using explicit knowledge of the commutator between H_0 and the particular operator in question.

The Schrödinger picture time-propagator is related to the interaction-picture time-propagator via (38), giving

$$U_S(t) = e^{-iH_0 t/\hbar} U_I(t), \tag{50}$$

thus if one calculated $U_I(t)$, one could readily determine $U_S(t)$. The advantage of calculating $U_I(t)$ instead of directly calculating $U_S(t)$ is that H_0 is removed from the equation of motion, i.e.

$$\frac{d}{dt} U_I(t) = V_I(t) U_I(t), \tag{51}$$

whereas

$$\frac{d}{dt} U_S(t) = (H_0 + V) U_S(t). \tag{52}$$

As the cost of dropping a term from the equation of motion is a simple multiplication by $e^{-iH_0 t/\hbar}$ at the end, it is well worth-it to use this approach.

3 The Perturbation Expansion

The advantage of using perturbation theory to calculate the time-propagator, $U(t)$, as opposed to the state-vector,$|\psi_(t)\rangle$, is that once it is computed, the state at time t is readily determined for *any* initial state via $|\psi(t)\rangle = U(t)|\psi(0)\rangle$. We note that it is customary to use the notation $U_0(t) = e^{-iH_0t/\hbar}$, i.e. $U_{SI}(t) \to U_0(t)$, as this operator is also the time-propagator of the unperturbed Hamiltonian (in the Schödinger picture).

To solve Eq. (51), we expand $U_I(t)$ as a power series in λ,

$$U_I(t) = U_I^{(0)}(t) + \lambda U_I^{(1)}(t) + \lambda^2 U_I^{(2)}(t) + \ldots, \tag{53}$$

and substitute this into the equation of motion,

$$\frac{d}{dt}\left(U_I^{(0)}(t) + \lambda U_I^{(1)}(t) + \lambda^2 U_I^{(2)}(t) + \ldots\right) = -\frac{i}{\hbar}V_I(t)\left(\lambda U_I^{(0)}(t) + \lambda^2 U_I^{(1)}(t) + \ldots\right). \tag{54}$$

Due to the linear independence of the terms in a power series, a general solution requires us to equate separately all terms with the same power. From the λ^0 terms, we get

$$\lambda^0: \qquad \frac{d}{dt}U_I^{(0)}(t) = 0, \tag{55}$$

This, together with the requirement that our solution holds for $\lambda = 0$, and our initial condition, $U_I(0) = I$, requires $U_I^{(0)}(t) = I$, while all other terms in the expansion must vanish at $t = 0$. This can be written compactly as

$$U_I{}^{(j)} = \delta_{j,0}. \tag{56}$$

At first-order we find

$$\lambda^1: \qquad \frac{d}{dt}U_I^{(1)}(t) = -\frac{i}{\hbar}V_I(t)U_I{}^{(0)} = -\frac{i}{\hbar}\int_0^t dt_1 V_I(t_1), \tag{57}$$

where we have used the zeroth order result. Formal integration gives

$$U_I^{(1)}(t) = -\frac{i}{\hbar}\int_0^t dt_1\, V_I(t_1). \tag{58}$$

At second order, we have

$$\lambda^2: \qquad \frac{d}{dt}U_I^{(2)}(t) = -\frac{i}{\hbar}V_I(t)U_I^{(1)}(t). \tag{59}$$

Again formal integration gives

$$\begin{aligned} U_I^{(2)}(t) &= -\frac{i}{\hbar}\int_0^t dt_2 V_I(t_2)U_I^{(1)}(t_2) \\ &= \left(\frac{-i}{\hbar}\right)^n \int_0^t dt_2 \int_0^{t_2} dt_1\, V_I(t_2)V_I(t_1) \end{aligned} \tag{60}$$

At this point the pattern is clear, and we can write our final result

$$U_I^{(j)}(t) = \left(\frac{-i}{\hbar}\right)^j \int_0^t dt_j \int_0^{t_j} dt_{j-1} \ldots \int_0^{t_3} dt_2 \int_0^{t_2} dt_1 V_I(t_j)V_I(t_{j-1})\ldots V_I(t_2)V_I(t_1). \tag{61}$$

The problem is now 'solved', what remains is to put the pieces together to compute 'transition probabilities', and to try to gain some intuition by 'interpreting' our result.

4 Switching back to the Schrödinger Picture

We have seen that

$$U_S(t) = U_{SI}(t)U_I(t) = e^{-iH_0t/\hbar}U_I(t). \tag{62}$$

Using $V_I(t) = U_0^\dagger(t)V(t)U(t)$, together with the fact that $U_0(t)U_0^\dagger(t') = U_0(t-t')$, we find

$$\begin{aligned} U_S(t) &= U_0(t) + \left(\frac{-i}{\hbar}\right)\lambda\int_0^t dt_1 U_0(t-t_1)V(t_1)U_0(t_1) \\ &+ \left(\frac{-i}{\hbar}\right)^2\lambda^2\int_0^t dt_2\int_0^{t_2} dt_1 U_0(t-t_2)V(t_2)U_0(t_2-t_1)V(t_1)U_0(t_1) \\ &+ \left(\frac{-i}{\hbar}\right)^3\lambda^3\int_0^t dt_3\int_0^{t_3} dt_2\int_0^{t_2} dt_1 U_0(t-t_3)V(t_3)U_0(t_3-t_2)V(t_2)U_0(t_2-t_1)V(t_1)U_0(t_1) \\ &+ \ldots, \end{aligned} \tag{63}$$

where we note that $0 < t_1 < t_2 < t_3 \ldots < t_j < t$, so that the time evolution in each term can be traced clearly from right to left. This shows that the time-propagator has a natural interpretation in terms of instantaneous 'quantum jumps'. The first term simply describes free propagation (i.e. governed by H_0 alone) of the initial state under the background Hamiltonian, H_0. The second term describes free propagation for a time t_1, followed by a sudden change of state from $|\psi(t_1)\rangle$ to the state $|\psi'\rangle = V(t_1)|\psi(t_1)\rangle$. After this 'jump', the new state continues to propagate freely from t_1 to t. By integrating over t_1, this term is a summation over all possible evolution 'paths' containing exactly one quantum jump. Likewise, the third term is a sum over all trajectories with two quantum jumps, and so on. Thus the full propagator is thus a sum over all possible quantum jump sequences.

5 Transition Amplitudes

Quantum mechanics is formulated to answer the question: "If the particle starts in state $|m\rangle$, what is the probability that it will be found in state $|n\rangle$ at time t?" The probability to be in state $|n\rangle$ at time t, given that the system was in state $|m\rangle$ at time $t = 0$, is given by

$$P_{n\leftarrow m}(t) = |\langle n|U_S(t)|m\rangle|^2 = |\langle n|U_0(t)U_I(t)|m\rangle|^2. \tag{64}$$

As we know, quantum mechanics is a theory of probability amplitudes rather than probabilities. Thus we will use our perturbation expansion for the interaction-picture propagator to directly compute the transition amplitudes. The probability amplitude for the system to be in state $|n\rangle$ at time t, given that it is state $|m\rangle$ at $t = 0$ is

$$u_{nm}(t) = \langle n|U_S(t)|m\rangle = \langle n|U_0(t)U_I(t)|m\rangle. \tag{65}$$

Henceforth we shall assume that both $|m\rangle$ and $|n\rangle$ are eigenstates of H_0, with eigenfrequencies ω_m and ω_n, respectively. With this, the amplitude becomes

$$u_{nm}(t) = e^{-i\omega_n t}\langle n|U_I(t)|m\rangle. \tag{66}$$

Since the $u_{nm}(t)$'s are computed with respect to the full Hamiltonian $H = H_0 + \lambda V(t)$, we can expand them in power series in λ as

$$u_{nm}(t) = u_{nm}^{(0)}(t) + \lambda u_{nm}^{(1)}(t) + \lambda^2 u_{nm}^{(2)}(t)\ldots \tag{67}$$

From the definition (65), and the perturbation expansion (61), it is easy to construct the terms in the series

$$u_{nm}^{(0)}(t) = e^{-\omega_n t}\delta_{nm} \tag{68}$$

$$u_{nm}^{(1)}(t) = -\frac{i}{\hbar}e^{-\omega_n t}\int_0^t dt_1 \langle n|V_I(t_1)|m\rangle \tag{69}$$

$$u_{nm}^{(2)}(t) = -\frac{1}{\hbar^2}e^{-\omega_n t}\sum_{m_2}\int_0^t dt_2 \int_0^{t_2} dt_1 \, \langle n|V_I(t_2)|m_2\rangle\langle m_2|V_I(t_1)|m\rangle, \tag{70}$$

and so on. Switching back to the Schrödinger picture via

$$\langle n|V_I(t)|m\rangle = \langle n|U_0^\dagger(t)V_S(t)U_0(t)|m\rangle = \langle n|V_S(t)|m\rangle e^{i(\omega_n-\omega_m)t}, \tag{71}$$

and with the definition

$$V_{nm}(t) := \langle n|V_S(t)|m\rangle, \tag{72}$$

we can express the j^{th} term as

$$\begin{aligned} u_{nm}^{(j)}(t) &= \left(\frac{-i}{\hbar}\right)^j \sum_{\substack{m_2,\, m_3,\\ \ldots,\, m_j}} \int_0^t dt_j \int_0^{t_j} dt_{j-1} \ldots \int_0^{t_2} dt_1 \, e^{-i\omega_n(t-t_j)}V_{nm_j}(t_j)e^{-i\omega_{m_j}(t_j-t_{j-1})}V_{m_jm_{j-1}}(t_{j-1})\ldots \\ &\qquad \ldots e^{-i\omega_{m_3}(t_3-t_2)}V_{m_3m_2}(t_2)e^{-i\omega_{m_2}(t_2-t_1)}V_{m_2m}(t_1)e^{-i\omega_m(t_1)} \end{aligned} \tag{73}$$

This term can clearly be interpreted as the amplitude for the process where the system goes from bare-state $|m\rangle$ to bare-state $|n\rangle$ by a sequence of j discrete quantum jumps between bare eigenstates. The summations and integrations are then summing over all possible jump times and intermediate states. For the purposes of calculation, it is slightly more convenient to use $\omega_{nm} = \omega_n - \omega_n$,and write

$$\begin{aligned} u_{nm}^{(j)}(t) &= \left(\frac{-i}{\hbar}\right)^j \sum_{\substack{m_2,\, m_3,\\ \ldots,\, m_j}} \int_0^t dt_j \int_0^{t_j} dt_{j-1} \ldots \int_0^{t_2} dt_1 \, e^{-i\omega_n t}V_{nm_j}(t_j)e^{i\omega_{nm_j}t_j}V_{m_jm_{j-1}}(t_{j-1})e^{i\omega_{m_{j-1}m_{j-2}}t_2}\ldots \\ &\qquad \ldots V_{m_3m_2}(t_2)e^{i\omega_{m_2m}t_1} \end{aligned} \tag{74}$$

The probability to be found in state $|n\rangle$ at time t is given in terms of these amplitudes by

$$P_{n\leftarrow m}(t) = \left|\delta_{nm} + \lambda u_{nm}^{(1)}(t) + \lambda^2 u_{nm}^{(2)}(t)\ldots\right|^2 \tag{75}$$

It is important to appreciate that the transition probability is the square of the sum of the amplitudes and not the sum of the squares. The meaning of this is that the different pathways from $|m\rangle$ to $|n\rangle$ can interfere with each other constructively or destructively, and that this interference can have a significant effect on the transition probability.

The final key is to expand the *probability* to the desired order in λ, giving for $n \neq m$

$$P_{n\leftarrow m}(t) = \lambda^2|u_{nm}^{(1)}(t)|^2 + O(\lambda^3) \tag{76}$$

This makes the important point that **to calculate the transition probabilities between distinct quantum state to 2nd order, it is only necessary to compute the amplitudes to first order**. For the case $n = m$, this is no longer the case, however, it is much easier to derive it from conservation of probability, as opposed to direct integration. By conservation of probability, we have

$$P_{m\leftarrow m} = 1 - \lambda^2\sum_{n\neq m}|u_{nm}^{(1)}(t)|^2 + O(\lambda^3). \tag{77}$$

6 Harmonic Perturbations

Here we consider the case of a perturbation with a single well-defined frequency, whose perturbation operator is

$$V(t) = Ve^{-i\omega t} + V^\dagger e^{i\omega t}. \tag{78}$$

For $n \neq m$, the first order probability amplitudes are then

$$u_{nm}^{(1)}(t) = -\frac{i}{\hbar}e^{-i\omega_n t}\left[V_{nm}\int_0^t dt_1\, e^{-i(\omega-\omega_{nm})t_1} + V_{mn}^*\int_0^t dt_1\, e^{i(\omega+\omega_{nm})t_1}\right] \tag{79}$$

We can perform the integration, yielding

$$u_{nm}^{(1)} = -\frac{2i}{\hbar}\left[V_{nm}e^{-i(\omega+\omega_n+\omega_m)t/2}\frac{\sin\left((\omega-\omega_{nm})t/2\right)}{\omega-\omega_{nm}} + V_{mn}^* e^{i(\omega-\omega_n-\omega_m)t/2}\frac{\sin\left((\omega+\omega_{nm})t/2\right)}{\omega+\omega_{nm}}\right] \tag{80}$$

It is common to encounter the situation where the drive frequency is very close to the transition frequency, i.e.t $\omega \approx |\omega_{nm}|$. Note that while ω is a positive frequency by definition, the transition frequency ω_{nm} can be positive or negative, depending on the ordering of n and m.The near-resonance condition is therefore $\omega \approx |\omega_{nm}|$. This implies then that $\omega - |\omega_{nm}| \ll \omega + |\omega_{nm}|$. In this case, the far off-resonance term is smaller than the near-resonance term by a factor of $\frac{\omega-|\omega_{nm}|}{2|\omega_{nm}|}$. Thus it is usually justified to drop the non-resonant term, which can give a much smaller correction than say, the second-order near-resonant term. For example, in optics, we have $\omega \sim 10^{15}\mathrm{s}^{-1}$, whereas $\Delta = \omega - \omega_{nm} \sim 10^7\mathrm{s}^{-1}$, so that the far off-resonance term is smaller by a factor 10^{-8}. Keeping only the near-resonance term, the probability to be in state n at time t, given that the system was in state m at $t = 0$, is

$$P_{n\leftarrow m}(t) \approx \frac{4|V_{nm}|^2}{\hbar^2}\frac{\sin^2\left((\omega-|\omega_{nm}|)t/2\right)}{(\omega-|\omega_{nm}|)^2}. \tag{81}$$

In the exactly on-resonance cas,e $\omega = |\omega_{nm}|$, we can take the limit $\omega \to |\omega_{nm}|$ of this expression, giving

$$P_{n\leftarrow m}(t) \approx \frac{|V_{nm}|^2}{\hbar^2}t^2. \tag{82}$$

For the decay of the initial state, conservation of probability gives

$$P_{m\leftarrow m}(t) = 1 - \sum_{n\neq m} P_{m\to n}(t) = 1 - \sum_{n\neq m}\frac{4|V_{nm}|^2}{\hbar^2}\frac{\sin^2\left((\omega-|\omega_{nm}|)t/2\right)}{(\omega-|\omega_{nm}|)^2}. \tag{83}$$

To evaluate this term, some judgement must be made whether to keep or discard the counter-rotating term in (80). Keep in mind that the summation of a large number of negligible terms may or may not be negligible, depending on the specific form of the terms involved. Note that for short times, we must have, for short times,

$$\sum_{n\neq m} P_{m\to n}(t) \propto t^2, \tag{84}$$

as can be seen from (82).

7 The problem of a single state coupled to a continuum of final states: Fermi's Golden Rule

An interesting result occurs when there are many available final states all very close to resonance. If the levels are close enough, they form a quasi continuum and we can replace the summation by an integral,

$$\sum_{n=n_{min}}^{n_{max}} d_n \to \int_{E_{min}}^{E_{max}} dE\, n(E), \tag{85}$$

where n is the principle quantum number, d_n is the degeneracy of the n^{th} energy level, and $n(E)$ is the 'density of states', defined by

$$n(E) = \frac{dN(E)}{dE}, \tag{86}$$

with $N(E)$ being the number of possible final states with energies below E. Note that both sides of (85) yield $N(E_{max})$ upon summation/integration, with the understanding that $E_{max} = \hbar\omega_{n_{max}}$ in the discrete case.

Let us now consider the simplest case where a single level $|m\rangle$ is coupled to a continuum, with time-independent coupling constants, i.e. $\omega = 0$, or equivalently

$$V(t) = V. \tag{87}$$

As long as we are trying to compute $|\psi(t)\rangle$, we can still use TDPT. In this case, we can write the probability to remain in state m, in the continuum limit, as

$$P_{m\to m}(t) = 1 - \lambda^2 4 \int dE_f\, n(E_f)|V_m(E_f)|^2 \frac{\sin^2((E_f - \hbar\omega_m)t/2\hbar)}{(E_f - \hbar\omega_m)^2}, \tag{88}$$

where we have taken $\hbar\omega_n \to E_f$, and $V_{nm} \to V_m(E_f)$, to emphasize that we are integrating over final states.

Mathematically speaking, the function $\sin^2(ax)/x^2$ is an element of a delta-sequence, so that

$$\lim_{a\to\infty} \frac{\sin^2(ax)}{x^2} = \pi a \delta(x). \tag{89}$$

To see this, note that its maximum value, occuring at $x = 0$ is a, and that it is bounded from above by the envelope function

$$f(x) = \frac{1}{a} \cdot \frac{1}{x^2}, \tag{90}$$

which goes to zero as $a \to \infty$ for all $x \neq 0$. In addition, its integral is independent of a,

$$\int_{-\infty}^{\infty} dx\, \frac{\sin^2(ax)}{x^2} = \int_{-\infty}^{\infty} du\, \frac{\sin^2 u}{u^2} = \pi. \tag{91}$$

Thus in the limit as $a \to 0$, the height at $x = 0$ goes to ∞, while the value for all $x \neq 0$ goes to zero, with the area held constant. With $a = t/2\hbar$ and $x = E_f - \hbar\omega_i$, we thus have

$$\lim_{t\to\infty} \frac{\sin^2((E_f - \hbar\omega_m)t/2\hbar)}{(E_f - \hbar\omega_m)^2} = \frac{\pi t}{2\hbar}\delta(E_f - \hbar\omega_m) \tag{92}$$

For t large compared to the inverse bandwidth, i.e. $t \ll \hbar/(E_{max} - E_{min})$, we then have

$$\begin{aligned} P_{m\to m}(t) &\approx 1 - \frac{2\pi t}{\hbar}\int dE\, n(E)|V_m(E)|^2\delta(E-\hbar\omega_m) \\ &\approx 1 - \frac{2\pi}{\hbar}|V_m(E_m)|^2 n(E_m)\, t \\ &\approx 1 - \Gamma\, t, \end{aligned} \tag{93}$$

This shows that the probability to remain in the initial state $|m\rangle$ decays at the rate

$$\Gamma = \frac{2\pi|V_m(E_m)|^2 n(E_m)}{\hbar}. \tag{94}$$

This result is known as the 'Fermi Golden Rule', and is a handy way to estimate the decay rate when probability flows from a small quantum system o a much larger system. The physics of the irreversibility is that the reverse processes from all of the different final states interfere with random phases, and thus cancel each other out. This requires sufficient time to have passed for the the continuum states to randomize their phases, hence the requirement $t \gg \hbar/(E_{max} - E_{min})$.

The Fermi golden rule is more conventionally written as

$$\Gamma = \frac{2\pi}{\hbar}|V_{fi}|^2 n(E_i). \tag{95}$$

where E_i is the energy of the initial state, and V_{fi} is the matrix element coupling the initial state to the final state, where the final state is selected by energy conservation. In order for first-order perturbation theory to be valid, we therefore require that the deviation from the unperturbed value, i.e. unity, be a small perturbation, thus the validity of the FGR is

$$\frac{\hbar}{E_{max} - E_{min}} \ll t \ll \frac{1}{\Gamma}. \tag{96}$$

Note that the result (93) seems to violate the quadratic condition (84), but we shouldn't be alarmed, because (84) is valid for $t \lesssim \hbar/(E_{max} - E_{min})$, whereas the FGR is expected to break-down.