Chapter 5

Time-dependent perturbation theory

5.1 Introduction

Postulate 2 of quantum mechanics tells us that if we wish to determine the time-evolution of a quantum system we solve the time-dependent Schrödinger equation (TDSE)

$$i\hbar\frac{\partial|\psi\rangle}{\partial t} = \hat{H}|\psi\rangle \tag{5.1}$$

where $\hat{H}$ is the Hamiltonian operator, a Hermitian operator which specifies the full dynamics of the system.

If the Hamiltonian is constant in time, and if we know its spectral decomposition (eigenvalues E_k and eigenvectors $|\phi_k\rangle$), we can integrate the Schrödinger equation for any initial state expressed in terms of orthonormal eigenvectors of $\hat{H}$. i.e.

$$|\psi(t)\rangle = \sum_k \exp\left[\frac{-iE_k t}{\hbar}\right] c_k|\phi_k\rangle \tag{5.2}$$

In many systems of interest, however, we are not so lucky. Either a) we possess no method for diagonalising the Hamiltonian (often the case, for example with interacting many-body systems) or b) the Hamiltonian is not constant in time. Fortunately, in a remarkably broad range of cases, we find Hamiltonians which are *close* to ones we can solve exactly.

Perturbation theory is the name of a set of techniques, where the problem in question may be seen as a *small perturbation* away from a problem which we do

know how to solve, and where the solutions are close, up to small corrections, to the exact solutions of the solvable problem. Perturbation theory provides methods for calculating these corrections, which often describe important phenomena in the physics of the problem.

You are likely to have encountered time-*independent* perturbation theory in your previous courses[1]. This is used to study problems where $\hat{H}$ is constant in time, but where we do not know how to exactly calculate its eigenvectors and eigenvalues. In this chapter, you will study *time dependent* perturbation theory, used to approximate the dynamics of a problem when either a) or b) or both of the above criteria do not hold. Time-dependent perturbation theory has had many applications in quantum theory, and plays an important role in many fields of physics, e.g from atomic physics to laser physics, from particle physics to quantum field theory.

Statement of the problem

Consider a system described by the following Hamiltonian

$$\hat{H}(t) = \hat{H}_0 + \lambda \hat{V}(t) \tag{5.3}$$

where $\hat{H}_0$ is a time-independent Hamiltonian, whose eigenvalues E_k and eigenvectors $|\phi_k\rangle$ are known, $\hat{V}(t)$ is a (usually time-dependent) Hamiltonian, and λ is a real number parameter which is introduced as a tool in our analysis, later we shall set $\lambda = 1$. Perturbation theory is effective when the perturbation $\hat{V}(t)$ is weak, which, loosely speaking, means that the energies involved in this Hamiltonian are much smaller than the energy scales of $\hat{H}_0$, or that the matrix elements of $\hat{V}_t$ are much smaller than the differences in energy $E_{j'} - E_j$.

Beware of the notation here, $\hat{V}$ is **not** a simple potential energy operator, and should not be associated with those simple spatial potential operators encountered in previous courses. $\hat{V}$ could be any Hamiltonian operator, but in practice it will often be a Hamiltonian associated with the interaction energy of two particles or degrees of freedom.

If no perturbation were present ($\hat{V}(t) = 0$) then we could solve the TDSE to obtain

$$|\psi(t)\rangle = \sum_k \exp\left[\frac{-iE_k t}{\hbar}\right] c_k |\phi_k\rangle \tag{5.4}$$

[1] If you did not, I recommend that you read chapter 8.1 in Bransden and Joachain's *Quantum Mechanics* as background to the present chapter.

as above.

Note that the coefficients c_k here are constant in time, and depend on the initial state

$$|\psi(0)\rangle = \sum_k c_k |\phi_k\rangle \tag{5.5}$$

The goal of time-dependent perturbation theory is to provide approximate solutions to the TDSE when perturbation $\hat{V}(t)$ is small, but non-zero.

5.2 Dirac's method (Interaction Picture)

Since $\hat{H}_0$ is solved, we would like to focus our attention on the effect on the dynamics of the perturbation term $\lambda\hat{V}$. We shall therefore work again in the interaction picture.

Let us represent the state, in the interaction picture in terms of the eigenstates of $\hat{H}_0$,

$$|\psi_I(t)\rangle = \sum_j c_j(t)|\phi_j\rangle. \tag{5.6}$$

If we transform this back to the Schrödinger picture, we see

$$|\psi_S(t)\rangle = U_0(t)|\psi_I(t)\rangle = \sum_j c_j(t) \exp\left[\frac{-iE_j t}{\hbar}\right] |\phi_j\rangle. \tag{5.7}$$

where $U_0(t) = \exp[-i\hat{H}_0 t/\hbar]$ and hence in the interaction picture, the state has the same form as equation (5.4) except the constants $c_j(t)$ are now time-varying. For this reason the method is sometimes called "Dirac's method of variation of constants".

We now solve the Schrödinger equation in the interaction picture

$$i\hbar\frac{\partial}{\partial t}|\psi_I(t)\rangle = U_0^\dagger(t)\lambda\hat{V}(t)U_0(t)|\psi_I(t)\rangle \tag{5.8}$$

substituting in the decomposition in equation (5.6), we obtain

$$i\hbar\frac{\partial}{\partial t}\sum_j c_j(t)|\phi_j\rangle = \lambda U_0^\dagger(t)\hat{V}(t)U_0(t)\sum_k c_k(t)|\phi_k\rangle \tag{5.9}$$

If we multiply from the left with $\langle\phi_m|$, using $\langle\phi_m|\phi_k\rangle = \delta_{m,k}$ and writing $V_{mk} = \langle\phi_m|\hat{V}|\phi_k\rangle$ (this is a matrix element for $\hat{V}$) we obtain

$$\dot{c}_m(t) = \frac{\lambda}{i\hbar}\sum_k c_k(t)\exp\left[i\omega_{mk}t\right]V_{mk}(t) \tag{5.10}$$

where $\omega_{mk} = (E_m - E_k)/\hbar$ is called the Bohr angular frequency.

Equation (5.10) is precisely equivalent to the time-dependent Schrödinger equation. We have not made any approximations yet. It is a series of coupled differential equations for the coefficients $c_m(t)$, which, if one could solve them, would provide an exact solution to the TDSE. Note that the operator $\hat{H}_0$ does not appear in equation (5.10). This is a key strength of Dirac's interaction picture approach. Since the time-evolution due to $\hat{H}_0$ alone is already explicitly taken care of in the interaction picture, one can focus ones attention solely at the perturbation $\lambda\hat{V}(t)$, which significantly simplifies the equations used.

In many cases (5.10) cannot be solved exactly, but, provided the perturbation is weak enough, a perturbative expansion of $c_m(t)$ can be effective with only a small number of terms.

5.3 Perturbative expansion

We shall express $c_m(t)$ as a power series in λ:

$$\begin{aligned} c_m(t) =& c_m^{(0)}(t) + \lambda c_m^{(1)}(t) + \lambda^2 c_m^{(2)}(t) + \cdots \\ =& \sum_j \lambda^j c_m^{(j)}(t). \end{aligned} \tag{5.11}$$

Substituting this expression into (5.10) we obtain

$$\frac{\partial}{\partial t}\left[\sum_j \lambda^j c_m^{(j)}(t)\right] = \frac{\lambda}{i\hbar}\sum_k \exp\left[i\omega_{mk}t\right]V_{mk}(t)\sum_n \lambda^n c_k^{(n)}(t) \tag{5.12}$$

This expression should hold for any value of λ, and hence terms on the LHS associated with λ^p must be equal to terms associated with λ^p on the RHS. Equating powers of λ gives rise to a hierarchy of differential equations:

To derive an expression for *0th-order* terms, we identify terms to zeroth power in λ. On the left-hand side that leaves us $j = 0$ on the right-hand-side no term satisfies this, since all are multiplied by the λ outside the sum, and hence,

$$\dot{c}_m^{(0)}(t) = 0 \tag{5.13}$$

An expression for *1st-order* terms may be obtained by considering λ^1, i.e. $j = 1$, $n = 0$:

$$\dot{c}_m^{(1)}(t) = \frac{1}{i\hbar} \sum_k \exp\left[iw_{mk}t\right] V_{mk}(t) c_k^{(0)}(t) \tag{5.14}$$

Similarly for *2nd-order* terms, we consider λ^2, i.e. $j = 2$, $n = 1$

$$\dot{c}_m^{(2)}(t) = \frac{1}{i\hbar} \sum_k \exp\left[iw_{mk}t\right] V_{mk}(t) c_k^{(1)}(t) \tag{5.15}$$

Repeating this process we see that, in general, the n-th order equation will have the form

$$\dot{c}_m^{(n)}(t) = \frac{1}{i\hbar} \sum_k \exp\left[iw_{mk}t\right] V_{mk}(t) c_k^{(n-1)}(t) \tag{5.16}$$

Note that from equation (5.13) the zero-order terms are constant in time, and also that if we set $\lambda = 0$ we recover the unperturbed Hamiltonian, and equation (5.11) reduces to the the $0th$-order solution. This means that the zeroth order coefficients are equal to the unperturbed solution.

Note also that the expressions above are independent of λ. They therefore hold even if we set $\lambda = 1$ and write

$$\begin{aligned} c_m(t) =& c_m^{(0)}(t) + c_m^{(1)}(t) + c_m^{(2)}(t) + \cdots \\ =& \sum_j c_m^{(j)}(t). \end{aligned} \tag{5.17}$$

It is natural to ask whether such a series (with $\lambda = 1$) will even converge. However, provided the perturbation is sufficiently weak, we find that this series does provide a good approximation to the true state even after just a small number of terms. In practice, in surprisingly many cases, perturbation theory works extremely well even to just to the first or second order correction. This means that the results of first and second order perturbation theory are utilised widely in physics.

5.4 First-order term

In the following sections we shall simplify our analysis by assuming that the perturbation is only "switched on" at a certain time $t = 0$, and that prior to that moment, the system is in an eigenstate $|\phi_j\rangle$ of the unperturbed Hamiltonian $\hat{H}_0$. This assumption fits many scenarios where time-dependent perturbation theory is employed.

If we did need to study an initial state in a superposition of eigenstates, we can do this via a modification of the below methods since, if $U(t)$ is the unitary time evolution operator describing the quantum evolution,

$$U \sum_j \alpha_j |\phi_j\rangle = \sum_j \alpha_j \left(U|\phi_j\rangle\right) \tag{5.18}$$

and hence one could solve the more general case, by calculating the evolution of individual initial eigenstates $|\phi_j\rangle$ and noticing that the state at time t is simply the superposition of the evolved eigenstates $\left(U|\phi_j\rangle\right)$.

Here, however, for simplicity, we assume that at time $t = 0$, $|\psi(t)\rangle = |\phi_j\rangle$, the eigenstate of $\hat{H}_0$ with energy E_0. This allows us to immediately solve for the zeroth-order solution. At time $t = 0$, when the perturbation is (instantaneously) switched on, the evolution will still (for an instant), satisfy the unperturbed Hamiltonian, and the unperturbed solution holds. This means that for $t = 0$ only the zero-th order terms are non-zero. Since the initial state is $|\phi_j\rangle$, the zeroth order terms must then be:

$$c_m^{(0)}(t) = \delta_{m,j}. \tag{5.19}$$

Let us now turn our attention to the first order terms. We can substitute equation (5.19) into equation (5.14) to obtain a differential equation which we can integrate:

$$\dot{c}_m^{(1)}(t) = \frac{1}{i\hbar} \exp\left[iw_{mj}t\right] V_{mj}(t). \tag{5.20}$$

Let us consider the $m = j$ coefficient and $m \neq j$ coefficients separately, and integrate between time $t = 0$ and time $t = \tau$, to give the first order term at $t = \tau$. First, for $m = j$

$$c_j^{(1)}(\tau) = \frac{1}{i\hbar} \int_0^\tau dt\, V_{jj}(t) \tag{5.21}$$

and for $m \neq j$

$$c_m^{(1)}(\tau) = \frac{1}{i\hbar} \int_0^\tau dt\, V_{mj}(t) \exp\left[iw_{mj}t\right]. \tag{5.22}$$

If the matrix elements of the perturbation $\hat{V}(t)$ are known, we can integrate these expressions to calculate these coefficients.

When the perturbation is sufficiently weak, the first order solution can be a good approximation to the exact solution, and

$$c_m(\tau) \approx \delta_{j,m} + c_m^{(1)}(\tau) \tag{5.23}$$

where we have written the zeroth order term explicitly.

Note that, if $c_m^{(1)}(\tau)$ for $m \neq j$ is non-zero, this indicates that there is a non-zero probability that the system, if measured at time τ will be found in state $|\phi_m\rangle$. We call this probability the *transition probability* $P_{j\to m}$ and write

$$P_{j\to m}^{(1)}(\tau) = |c_m^{(1)}(\tau)|^2 \tag{5.24}$$

where the superscript $^{(1)}$ denotes that this is a first order approximation.

On the other hand $|1 + c_j^{(1)}(\tau)|^2$ represents the probability that the system remains in the initial state $|\phi_j\rangle$. We expect, if the perturbation is weak, that this will stay close to 1. Comparing, $c_j(\tau)$ to first order

$$\begin{aligned} c_j(\tau) &\approx 1 + c_j^{(1)} \\ &= 1 + \frac{1}{i\hbar}\int_0^\tau dt\, V_{jj}(t) \end{aligned} \tag{5.25}$$

with an exponential function expanded to first order

$$\exp[\frac{-i}{\hbar}\int_0^\tau dt\, V_{jj}(t)] \approx 1 + \frac{-i}{\hbar}\int_0^\tau dt\, V_{jj}(t) \tag{5.26}$$

we see that to first order, the correction to $c_j(\tau)$ due to the perturbation is equivalent to a phase shift

$$c_j(\tau) \approx e^{i\phi} c_j(0) \tag{5.27}$$

where

$$\phi = \frac{-1}{\hbar}\int_0^\tau dt\, V_{jj}(t) \tag{5.28}$$

This implies that the probability that the system will remain in its initial state is close to one, and that the first order transition probabilities will be small.

5.5 Second order correction

In some cases, the perturbation will be strong enough that the second order terms are required to get a good approximation. Once first-order terms have been derived, we may substitute them into equation (5.15) to obtain explicit expressions for the second order terms. Let us continue our analysis of the case where the perturbation is switched on at time $t = 0$ and $|\psi(0)\rangle = |\phi_j\rangle$.

Recall that

$$\dot{c}_m^{(2)}(t) = \frac{1}{i\hbar} \sum_k \exp\left[iw_{mk}t\right] V_{mk}(t) c_k^{(1)}(t) \tag{5.29}$$

Substituting in the first order terms we derived above (equation (5.22)) and integrating, we obtain

$$\begin{aligned} c_m^{(2)}(\tau) = & \frac{-1}{\hbar^2} \int_0^\tau dt' \int_0^{t'} dt \sum_k \exp\left[iw_{mk}t'\right] \\ & \times \exp\left[iw_{kj}t\right] V_{mk}(t') V_{kj}(t) \end{aligned} \tag{5.30}$$

There are several remarks to make on the structure of these second order terms. Notice the double time integral, first over variable t and then over t'. In general, due to repeated integration, an n-th order correction term will contain an n-fold time integral. Notice also the matrix elements of $\hat{V}$ involved are of the form. $V_{mk}(t')V_{kj}$, which we can write $\langle\phi_m|\hat{V}|\phi_k\rangle\langle\phi_k|\hat{V}|\phi_j\rangle$. Notice that this is the product of elements associated with two processes, first the transition from $|\phi_j\rangle$ to $|\phi_k\rangle$ and then the transition from $|\phi_k\rangle$ to $|\phi_m\rangle$. Thus, even if the first order term for the transition V_{mj} is zero, and there is no direct coupling between states, $|\phi_j\rangle$ to $|\phi_m\rangle$ can still take place at the level of second order terms, if a transition via a third state is possible.

5.6 Example: A constant perturbation

Some of the power of time-dependent perturbation theory is that some very general features of quantum processes may be seen in some simple examples. The first such example we shall consider is a perturbation which is constant in time. We assume that the perturbation is switched on at time $t = 0$, and that this "switching on" represents the only time-variation in the Hamiltonian. In other words, the Hamiltonian $\hat{H}$ can be written

$$\hat{H} = \begin{array}{ll} \hat{H}_0 & t < 0 \\ \hat{H}_0 + \hat{V} & 0 \leq t < \tau. \end{array} \tag{5.31}$$

We shall assume that the system is measured at time $t = \tau$ and that we are not interested in the dynamics of the system after that time. Importantly the operator $\hat{V}$ is constant in time.

As before, we shall simplify our analysis by assuming that at time $t = 0$ the system is in an eigenstate of $\hat{H}_0$, $|\phi_j\rangle$ corresponding to an energy E_j. We wish to approximate the evolution of this state in time, $|\psi(t)\rangle = \sum_m c_m(t) \exp[-iE_m t/\hbar]|\phi_m\rangle$, and hence find approximations to the coefficients $c_m(\tau)$ at time $t = \tau$ when the state is measured.

Let us first assume the perturbation is weak enough to work to first order. We can therefore utilise directly the expression obtained in section 5.4. Substituting a time independent perturbation $\hat{V}$ into equation (5.22) we obtain for $m \neq j$

$$c_m^{(1)}(\tau) = \frac{1}{i\hbar} \int_0^\tau dt\, V_{mj} \exp\left[i w_{mj} t\right] \tag{5.32}$$

which we can integrate:

$$\begin{aligned} c_m^{(1)}(\tau) =& \frac{V_{mj}}{i\hbar} \int_0^\tau dt\ \exp\left[i w_{mj} t\right] \\ =& \frac{V_{mj}}{\hbar \omega_{mj}} \left[1 - \exp\left[i w_{mj} \tau\right]\right]. \end{aligned} \tag{5.33}$$

Note how this term is proportional to the ratio $V_{mj}/(\hbar\omega_{kj}) = V_{mj}/(E_k - E_j)$. Higher order corrections will be proportional to higher-order powers of such ratios. This motivates the claim that perturbation theory is applicable when the matrix elements of the perturbation Hamiltonian are much smaller than the difference in eigenvalues of $\hat{H}_0$. Physically speaking, this tells us that the energy scales associated with the perturbation are much smaller than the energy scales associated with $\hat{H}_0$, and this gives some intuition for the kinds of physical system in which perturbation theory can be appropriately deployed.

We can calculate first order transition probabilities from equation (5.33)

$$\begin{aligned} P^{(1)}_{j\to k}(\tau) &= |c^{(1)}_m(\tau)|^2 \\ &= \frac{|V_{mj}|^2}{\hbar^2}\frac{(1-\exp\left[iw_{mj}\tau\right])\left(1-\exp\left[-iw_{mj}\tau\right]\right)}{\omega^2_{kj}} \\ &= \frac{4|V_{mj}|^2}{\hbar^2}\frac{\sin^2(\omega_{kj}\tau/2)}{\omega^2_{kj}} \end{aligned} \tag{5.34}$$

where we have used the fact that $1-e^{ix} = e^{ix/2}(e^{-ix/2}-e^{ix/2}) = e^{ix/2}(-2i\sin(x))$. We shall write this expression

$$P^{(1)}_{j\to k}(\tau) = \frac{2|V_{mj}|^2}{\hbar^2}F(\tau,\omega_{kj}) \tag{5.35}$$

where

$$\begin{aligned} F(\tau,\omega) &= \frac{2\sin^2(\omega\tau/2)}{\omega^2} \\ &= \frac{\tau^2}{2}\frac{\sin^2(\omega\tau/2)}{(\omega\tau/2)^2} \\ &= \frac{\tau^2}{2}\text{sinc}^2(\omega\tau/2) \end{aligned} \tag{5.36}$$

We illustrate $F(\tau,\omega)$ in figure 5.1, plotted as a function of ω. Note the sinc-like shape of this function, dominated by one broad and high central peak, and other smaller peaks diminishing in height as you move away from $\omega = 0$. The height of the central peak is τ^2 and its full-width at half maximum is $\frac{2\pi}{\tau}$. Thus, as τ increases (i.e. the duration of the perturbation increases) the peak of this function gets narrower and taller. To describe it in the limit that τ gets very large, we require the Dirac δ-function.

Aside: Dirac delta function

You will have encountered the Dirac delta function in previous courses, so I will just summarise some of its properties here. It has a number of definitions, one of which, the *integral definition*

$$f(x) = \int_{-\infty}^{\infty} f(x')\delta(x-x')dx' \tag{5.37}$$

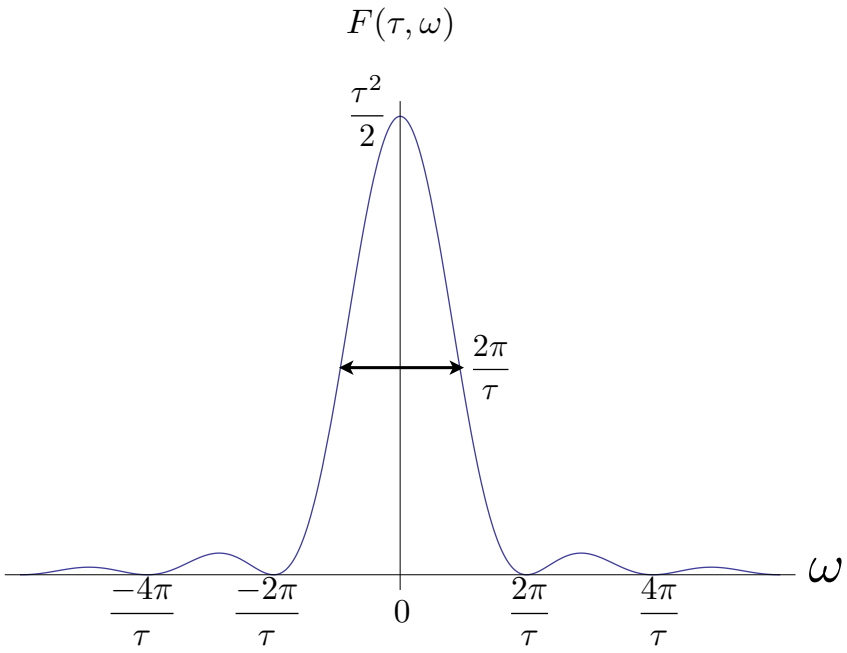

Figure 5.1: In this figure, the function $F(\tau, \omega)$ is plotted as a function of ω.

demonstrates the way that the delta function can be used to "remove" an integral, just as the standard delta (sometimes called Kronecker delta) $\delta_{j,k}$ allows us to remove summations. The Dirac delta function is not a true function, since its value on all inputs is not defined. It has a number of important properties

1. For $x \neq 0$ it takes the value $\delta(x) = 0$, for $x = 0$ the value of $\delta(x)$ is undefined ("infinite").

2. It satisfies:
$$\int_{-\infty}^{\infty} \delta(x)dx = 1 \tag{5.38}$$

3. and
$$\delta(ax) = \frac{1}{|a|}\delta(x) \tag{5.39}$$

The Dirac delta can be defined as the limiting value of many functions which have a sharp central peak, and which satisfy the property that, in some limit, the peak becomes narrow and high, and while the integral over x from $-\infty$ to $+\infty$ converges to 1.

A constant perturbation: continued

Returning to our analysis of a constant perturbation, we shall now see that $F(\tau, \omega_{kj})$ can, in the limit $\tau \to \infty$ be written in terms of a δ-function. Namely,

$$\lim_{\tau\to\infty} F(\tau, \omega) = \pi\tau\delta(\omega). \tag{5.40}$$

To see that this is reasonable, notice that in the limit that τ gets very large, the height of the central peak $(\tau^2/2)$ becomes large, while its width $(2\pi/\tau)$ gets small, at the same time, in this limit, the integral over ω behaves as follows:

$$\begin{aligned}
\int_{-\infty}^{\infty} \frac{F(\tau,\omega)}{\pi\tau} &= \frac{\tau}{2\pi}\int_{-\infty}^{\infty} \text{sinc}^2\left(\frac{\omega\tau}{2}\right) d\omega \\
&= \frac{\tau}{2\pi}\int_{-\infty}^{\infty} \frac{2}{\tau}\text{sinc}^2\left(x\right) dx \\
&= \frac{1}{\pi}\int_{-\infty}^{\infty} \text{sinc}^2\left(x\right) dx \\
&= \frac{\pi}{\pi} = 1
\end{aligned} \tag{5.41}$$

where we used a standard integral $\int_{-\infty}^{\infty} \text{sinc}^2(x)\, dx = \pi$. Notice that this integral is constant, and thus remains at this value in the limit $\tau \to \infty$ as required for a δ-function.

Perturbation Time-scales and Fermi's Golden Rule

If we return to consider the first order transition probabilities for the constant perturbation

$$P^{(1)}_{j\to k}(\tau) = \frac{2|V_{mj}|^2}{\hbar^2} F(\tau, \omega_{kj}) \tag{5.42}$$

we can see two different limits of behaviour, which hold independently of the operator $\hat{V}$ (i.e. independently of the physics of the problem). Recall that $\hbar\omega_{kj} = E_k - E_j$ represents the energy difference between initial and final states. For long perturbations, we can take the limit $\tau \to \infty$ and, in this limit, we can write equation (5.42)

$$P^{(1)}_{j\to k}(\tau) = \frac{2|V_{mj}|^2}{\hbar^2} \pi\tau\delta(\omega_{jk}) \tag{5.43}$$

which is zero unless $\hbar\omega_{kj} = E_k - E_j = 0$. In other words, in the long time limit, regardless of the form of $\hat{V}$, first order transitions can only occur between states of identical energy. This could be seen as a natural consequence of the conservation of energy.

On the other, hand, if we consider the small τ limit, we see for short perturbations a very different behaviour. In this limit $F(\tau, \omega_{kj})$ has a broad central peak, and thus transitions are allowed to states with a significant range of energies around E_j. To analyse this more quantitatively, let $\Delta\omega = 2\pi/\tau$ be the width of the central peak and let $\Delta t = \tau$ be the length of the perturbation.

Writing $\Delta E = \hbar\Delta\omega$ to represent the uncertainty in the energy of the final state after the transition we identify the relationship

$$\Delta E \Delta t = \hbar \tag{5.44}$$

This relationship reflects the time-energy uncertainty relation. It tells us that, over small time-scales quantum mechanics allows the energy of a system to be uncertain. Note that the energy-time uncertainty relation is of a fundamentally different kind to the standard Heisenberg uncertainty relation $\Delta x \Delta p \geq \hbar/2$ since unlike x and p, time t is not an observable. Nevertheless, the energy time uncertainty relation occurs in many physical phenomena such as the relationship between the line-width of radiation emitted from a transition and the natural decay rate of the transition.

Let us return now to the long time $\tau \to \infty$ limit. Notice that equation (5.43) is linear in time τ. We can therefore differentiate it to derive the transition rate

$$\Gamma^{(1)}_{j\to k}(\tau) = \frac{2\pi}{\hbar^2}|V_{mj}|^2\delta(\omega_{jk}) = \frac{2\pi}{\hbar}|V_{mj}|^2\delta(E_j - E_k) \tag{5.45}$$

This equation is called Fermi's Golden Rule. This rule, although approximate and derived using first-order perturbation theory, provides an accurate approximation of the transition rate of many physical processes, and is used as a useful rule-of-thumb to estimate transition rates before a more accurate calculation is made in many areas of physics, such as particle physics and atomic physics.

5.7 Harmonic Perturbation

In our previous example, the perturbation was assumed to be constant in time, but time-dependent perturbation theory can also treat perturbations which are time-varying. In this section, we shall consider the example of a harmonic perturbation, a perturbation $\hat{V}(t)$ varying sinusoidally in time. This is particularly important as it describes, to a first approximation, how atoms interact with light.

We can construct a rudimentary model of an atom by considering an electric dipole. An electric dipole consists of a pair of separated equal and opposite electric charges. We can think of our atom as a dipole formed by the positive nucleus surrounded by inner electrons, and the negative outer electron.

An electric dipole in an electric field $\vec{E}$ has the following potential energy

$$V = -\vec{E}\cdot\vec{D} \tag{5.46}$$

where $\vec{D}$ is the dipole moment.

Although this model is very naive, to a good first approximation, atoms do indeed interact with light like an electric dipole. For a fully quantum treatment, we would construct an atom-light interaction Hamiltonian from a quantum dipole operator and a quantum operator for the electromagnetic field (for more details see any quantum optics textbook). Here, however, we shall take a very simple approach and simply study the time-dependence of such an interaction.

Consider an atom interacting with a monochromatic laser. The E-field of the laser will be sinusoidal in time, ie $\vec{E}(t) = \vec{E}_0\cos(\omega t)$, where ω is the angular frequency of the radiation. The Hamiltonian representing the atom-light interaction will therefore have the form:

$$\hat{V} = \hat{H}_I\cos(\omega t) \tag{5.47}$$

where $\hat{H}_I$ is an operator which details the specific quantum description of the interaction (leading to transition rules etc.). We see that this Hamiltonian varies sinusoidally in time.

It is convenient to study a slightly more general family of harmonic Hamiltonians

$$\hat{V} = \hat{A}e^{i\omega t} + \hat{A}^\dagger e^{-i\omega t} \tag{5.48}$$

In the special case of A being a real symmetric matrix, this reduces to equation (5.47) with $\hat{H}_I = 2\hat{A}$.

As in previous examples, we shall label the unperturbed Hamiltonian $\hat{H}_0$ and assume that the perturbation is first "switched on" at time $t = 0$ and that prior to this time, the system is prepared in the state $|\phi_j\rangle$. For all times $t \geq 0$, the Hamiltonian will be

$$\hat{H} = \hat{H}_0 + \hat{A}e^{i\omega t} + \hat{A}^\dagger e^{-i\omega t}. \tag{5.49}$$

We can now use the results derived in earlier sections to calculate the coefficients of state $\sum_m c_m(t)|\phi_m\rangle$ to first order

$$c_m(t) \approx c_m^{(0)} + c_m^{(1)}(t) \tag{5.50}$$

As before, the 0-th order terms are determined by the initial condition $|\psi(t=0)\rangle = |\phi_j\rangle$,

$$c_m^{(0)} = \delta_{m,j} \tag{5.51}$$

The first order terms are given by equation (5.22)

$$c_m^{(1)}(\tau) = \frac{1}{i\hbar}\int_0^\tau dt\; V_{mj}(t)\exp\left[iw_{mj}t\right]. \tag{5.52}$$

If we substitute equation (5.48) into this expression we obtain

$$\begin{aligned} c_m^{(1)}(\tau) &= \frac{1}{i\hbar}\left[A_{mj}\int_0^\tau dt\; e^{i(\omega_{mj}+\omega)t} + (A)^\dagger_{mj}\int_0^\tau dt\; e^{i(\omega_{mj}-\omega)t}\right] \\ &= \frac{A_{mj}}{\hbar}\frac{1-e^{i(\omega_{mj}+\omega)\tau}}{\omega_{mj}+\omega} + \frac{A^*_{jm}}{\hbar}\frac{1-e^{i(\omega_{mj}-\omega)\tau}}{\omega_{mj}-\omega} \\ &= \frac{A_{mj}}{\hbar}\left(2i\tau e^{i(\omega_{mj}+\omega)\tau/2}\right)\mathrm{sinc}\left((\omega_{mj}+\omega)\tau/2\right) \\ &\quad + \frac{A^*_{jm}}{\hbar}\left(2i\tau e^{i(\omega_{mj}-\omega)\tau/2}\right)\mathrm{sinc}\left((\omega_{mj}-\omega)\tau/2\right) \end{aligned} \tag{5.53}$$

Just as for the case of a constant perturbation, the first order terms contain sinc functions from which in the limit $\tau >> 0$ will become Dirac delta functions. Via

an analysis similar to that in the previous section, one can show that the first term $\text{sinc}\left((\omega_{mj}+\omega)\tau/2\right)$ becomes proportional to $\delta(\omega_{mj}+\omega)$ and the second term $\text{sinc}\left((\omega_{mj}-\omega)\tau/2\right)$ becomes $\delta(\omega_{mj}-\omega)$.

In this limit, the first order coefficients will only be non-zero if one of two possible conditions are fulfilled, either a) $\omega_{mj}=\omega$ or b) $\omega_{mj}=-\omega$. These two cases correspond to conditions on the energies of the states $|\phi_m\rangle$ to which a transition can occur.

If case a) holds, $\omega_{mj}=\omega$ implies that $(E_m-E_j)/\hbar=\omega$ and thus $E_m=E_j+\hbar\omega$, i.e. the energy of the state $|\phi_m\rangle$ is one unit of $\hbar\omega$ higher than E_j. If case b) holds $\omega_{mj}=-\omega$ and therefore $E_m=E_j-\hbar\omega$, i.e. $|\phi_m\rangle$ is one unit of $\hbar\omega$ lower than E_j.

This means that first order perturbation theory has correctly predicted that light energy can only be absorbed by an atom in units of $\hbar\omega$ i.e. single photons. This is a remarkable result, since it was obtained with no detailed physical description of the atom-light interaction, and was achieved without even a full quantum mechanical treatment of light! A more comprehensive approach to atom-light interaction predicts similarly, absorption and stimulated emission, but also predicts a third kind of transition, missing from the simple treatment above, spontaneous emission of radiation, which can occur without any driving field.

In an analogous way to the constant perturbation, we can derive Fermi golden rules which describe the rate of transition from one state to another. These take a very similar form to the Fermi golden rule for a constant perturbation:

Absorption rate:

$$\Gamma^{(1)}_{j\to k}(\tau)=\frac{2\pi}{\hbar}|A_{kj}|^2\delta(E_k-E_j-\hbar\omega) \tag{5.54}$$

Emission rate:

$$\Gamma^{(1)}_{j\to k}(\tau)=\frac{2\pi}{\hbar}|A^*_{jk}|^2\delta(E_k-E_j+\hbar\omega) \tag{5.55}$$

Note that by swapping the labels j and k in equation (5.55) we obtain

$$\Gamma^{(1)}_{k\to j}(\tau)=\frac{2\pi}{\hbar}|A_{kj}|^2\delta(E_k-E_j-\hbar\omega) \tag{5.56}$$

where we used $\delta(x)=\delta(-x)$ and $|A^*_{kj}|^2=|A_{kj}|^2$.

This means that the rate of stimulated emission from state k to state j is equal to the rate of absorption from j to k. This is an example of "detailed balance", where the rate of a process is equal to the rate of an opposite process. Detailed balance applies in many examples in physics and can be a useful calculation tool.