5 Time–dependence

5.1 Time–dependent Hamiltonians

Recall that for a system described by a Hamiltonian, $\hat{H}_0$, which is time–independent, the most general state of the system can be described by a wavefunction $|\Psi, t\rangle$ which can be expanded in the energy eigenbasis $\{|n\rangle\}$ as follows:

$$|\Psi, t\rangle = \sum_n c_n \, \exp(-iE_n t/\hbar)\,|n\rangle$$

where the coefficients, c_n, are time-independent, and E_n denotes the eigenvalue corresponding to the energy eigenstate $|n\rangle$ of $\hat{H}_0$.

When we generalise to the case where the Hamiltonian is of the form

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

we can again expand in $|n\rangle$, the time-independent eigenbasis of $\hat{H}_0$

$$|\Psi, t\rangle = \sum_n c_n(t) \, \exp(-iE_n t/\hbar)\,|n\rangle$$

but the coefficients, c_n, will now in general be time-dependent.

The wavefunction satisfies the time-dependent Schrödinger equation;

$$i\hbar\frac{\partial}{\partial t}|\Psi, t\rangle = \hat{H}|\Psi, t\rangle$$

so that we can substitute the expansion of $|\Psi, t\rangle$ to determine the equations satisfied by the coefficients $c_n(t)$. Writing $E_n = \hbar\omega_n$ and denoting the time derivative of c_n by $\dot{c}_n$ we obtain

$$i\hbar\sum_n(\dot{c}_n - i\omega_n c_n)\exp(-i\omega_n t)|n\rangle = \sum_n(c_n\hbar\omega_n + c_n\hat{V})\exp(-i\omega_n t)|n\rangle$$

which simplifies immediately to give

$$\sum_n(i\hbar\dot{c}_n - c_n\hat{V})\exp(-i\omega_n t)|n\rangle = 0$$

We now premultiply this equation with another eigenstate of $\hat{H}_0$, $\langle m|$, to give

$$i\hbar\dot{c}_m \exp(-i\omega_m t) - \sum_n c_n V_{mn}\exp(-i\omega_n t) = 0$$

giving the following set of coupled, first–order differential equations for the coefficients:

$$\boxed{i\hbar\dot{c}_m = \textstyle\sum_n c_n V_{mn}\exp(i\omega_{mn} t)}$$

where $\omega_{mn} = \omega_m - \omega_n$ and $V_{mn} = \langle m|\hat{V}|n\rangle$.

This tells us how the coefficient c_m varies with time, i.e. the probability that a measurement will show the system to be in the m^{th} eigenstate. It is exact, but not terribly useful because we must, in general, solve an infinite set of coupled differential equations.

It is worth dwelling on the importance of the quantity V_{mn}. This ‘matrix element’ is an integral which tells us how much the potential $\hat{V}$ mixes states $|m\rangle$ and $|n\rangle$. If it is zero (which it often is, by symmetry) then $\hat{V}$ cannot induce a transition between states $|m\rangle$ and $|n\rangle$.

5.2 Time-dependent Perturbation Theory

Consider the Hamiltonian

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

where the time dependent part is *small.* We can write the time dependent coefficients c_n

$$c_n(t) = c_n(0) + \Delta c_n(t)$$

Where $c_n(0)$ is the value of c_n at t=0. We substitute in the equation for $\dot{c}_m$ derived above to give

$$\dot{c}_m(t) = (i\hbar)^{-1} \sum_n [c_n(0) + \Delta c_n(t)] V_{mn} \exp(i\omega_{mn} t)$$

We can assume that for a perturbation $c_n(0) >> \Delta c_n(t)$, and ignore the second term. This allows us to obtain the coefficients $c_m(t)$ by integrating the first–order differential equation to give:

$$c_m(t) = (i\hbar)^{-1} \sum_n c_n(0) \int_0^t V_{mn} \exp(i\omega_{mn} t)\, \mathrm{dt}$$

In the special case where the system is known to be in an eigenstate of $\hat{H}_0$, say $|k\rangle$, at $t = 0$, then $c_k(0) = 1$ and all other $c_m(0) = 0$, $m \neq k$, giving

$$c_m(t) = (i\hbar)^{-1} \int_0^t V_{mk} \exp(i\omega_{mk} t)\, \mathrm{dt}$$

Thus a system starting in a known eigenstate of the unperturbed system may transform to a different eigenstate through the action of the perturbing potential. Notice that $c_m(t)$ is an integral over time, if we wait a long time, the transition may become more likely.

The probability of finding the system at a later time, t, in the state $|m\rangle$ where $m \neq k$ is given by

$$p_m(t) = |c_m(t)|^2$$

Since we have assumed a small perturbation, this result is only reliable if $p_m(t) \ll 1$. "Small" here applies to both V_{mk} *and* its integral over time.

5.3 Time–independent Perturbations

The results obtained in the last section can also be applied to the case where the perturbation, $\hat{V}$, is actually independent of time (strictly, 'switched on' at t=0).

Again, starting the system in eigenstate $|k\rangle$ of $\hat{H}_0$ we obtain,

$$\begin{aligned} c_m(t)\Delta c_m(t) &= (i\hbar)^{-1} V_{mk} \int_0^t \exp(i\omega_{mk} t)\, \mathrm{dt} \\ &= \frac{V_{mk}}{\hbar\omega_{mk}} [1 - \exp(i\omega_{mk} t)] \end{aligned}$$

for $m \neq k$, giving for the transition probability

$$p_m(t) = |\Delta c_m(t)|^2 = \frac{|V_{mk}|^2}{\hbar^2} \frac{\sin^2(\omega_{mk} t/2)}{(\omega_{mk}/2)^2}.$$

For sufficiently large values of t, the function

$$f(t, \omega_{mk}) \equiv \frac{\sin^2(\omega_{mk} t/2)}{(\omega_{mk}/2)^2}$$

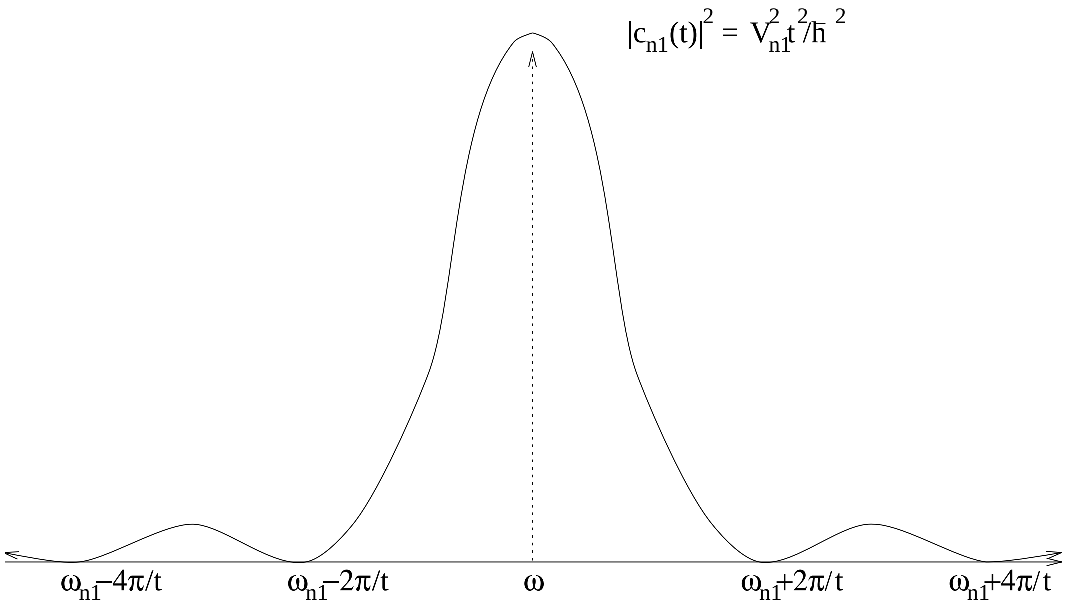

Figure 4: Transition probability as a function of applied harmonic perturbation frequency

consists essentially of a large peak, centred on $\omega_{mk} = 0$, of height t^2 and width $\approx 4\pi/t$, as indicated in Fig. 4. Thus there is only a significant transition probability if $E_m \approx E_k$. That is, if $|\omega_{mk}| < 2\pi/t$.

Note that we are assuming that the system was prepared in some eigenstate of $\hat{H}_0$ which is not an eigenstate of $\hat{V}$: if it were, then the matrix element V_{nm} would be zero and $p_m(t) = 0$. Thus although the analysis treats the perturbation as time independent, it is applied to cases where the perturbation is switched on at $t = 0$. Moreover only perturbations which are incompatible with the Hamiltonian can induce transitions.

5.4 Harmonic Perturbation

This is generally useful since by Fourier analysis we can decompose any periodic perturbation into harmonic components.

Let the perturbing potential be $V(\mathbf{r}, t) = V(\mathbf{r}) \cos \omega t$

If the initial state at $t = 0$ is k, and the final state m then

$$c_m \approx \frac{-i}{\hbar} V_{mk} \int_0^t e^{i\omega_{mk}t} \frac{1}{2}(e^{iwt} + e^{-iwt}) dt = \frac{V_{mk}}{2\hbar} \left(\frac{e^{i(\omega_{mk}-\omega)t} - 1}{\omega_{mk} - \omega} + \frac{e^{i(\omega_{mk}+\omega)t} - 1}{\omega_{mk} + \omega} \right)$$

where V_{mk} is the time independent part of the matrix element $\langle m|\hat{V}|k\rangle$. This function is dominated by the first term in the region around $\omega_{mk} = \omega$, so we can consider only the first term to obtain an estimate for the transition probability:

$$|c_m(t)|^2 = \frac{V_{mk}^2 \sin^2[(\omega_{mk} - \omega)t/2]}{\hbar^2 (\omega_{mk} - \omega)^2} = \frac{1}{4\hbar^2} V_{mk}^2 f(t, \omega_{mk} - \omega)$$

Where the function f is the same as we encountered earlier. Thus an external perturbation at a given frequency most strongly induces transitions between energy levels separated by $\hbar\omega$.

This is another manifestation of an uncertainty principle. If the potential is electromagnetic, the most probable transition is the absorption of a $\hbar\omega_{mk}$ photon as the system changes energy by

$\hbar\omega_{mk}$. But if the transition happens very fast, the peak is broad and the photon could have a wide range of energies, contrariwise, if the transition occurs after a long time the photon frequency is well defined: $\Delta E \Delta t \geq \hbar/2$. This uncertainty gives rise to the 'natural linewidth' of a particular transition, and causes a limit to the accuracy of certain experiments. There is a slight difference from the Heisenberg Uncertainty in non-relativistic quantum mechanics because time is not an operator so one cannot define the commutator of time with the Hamiltonian.

Note the extraordinary result that the transition probability at small times is $\left(V_{mk}^2/4\hbar^2\right) t^2$. Consider what happens if the state is measured frequently compared to if measurements are made infrequently: frequent measurement tends to inhibit the transition!

5.5 Transitions to a group of states

We are often interested in the situation where transitions take place not to a single final state but to a group, G, of final states with energy in some range about the initial state energy

$$E_k - \Delta E \leq E_m \leq E_k + \Delta E$$

Then the total transition probability is obtained by summing the contributions of all the final states. The number of final states in the interval between E_m and $E_m + \mathrm{dE_m}$ is $g(E_m)\,\mathrm{dE_m}$, where the function $g(E_m)$ is known as the *density of final states*. The total transition probability for transitions to G is then given by

$$p_G(t) = \frac{1}{\hbar^2}\int_{E_k-\Delta E}^{E_k+\Delta E} |V_{mk}|^2 f(t,\omega_{mk})\, g(E_m)\,\mathrm{dE_m}.$$

For sufficiently large t, and $\Delta E \gg 2\pi\hbar/t$, we observe that essentially the only contributions to the integral come from the energy range corresponding to the narrow central peak of the function $f(t,\omega_{mk})$. Within this range we can neglect the variation of $g(E_m)$ and V_{mk}, which can therefore be taken out of the integral to give

$$p_G(t) = \left[\frac{|V_{mk}|^2}{\hbar^2}\, g(E_m)\right]_{E_m=E_k} \int_{E_k-\Delta E}^{E_k+\Delta E} f(t,\omega_{mk})\,\mathrm{dE_m}.$$

Furthermore, we can extend the limits on the integration to $\pm\infty$. Noting that $\mathrm{dE_m} = \mathrm{\hbar\, d\omega_{mk}}$ and using the result that

$$\int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2}\,\mathrm{dx} = \pi$$

we obtain for the first–order transition probability

$$p_G(t) = \frac{2\pi t}{\hbar}\left[|V_{mk}|^2\, g(E_m)\right]_{E_m=E_k}$$

The transition rate, R, is just the derivative of this with respect to t and is thus given by the so–called Fermi Golden Rule:

$$R = \frac{2\pi}{\hbar}\left[|V_{mk}|^2\, g(E_m)\right]_{E_m=E_k}$$

The Fermi Golden Rule is probably the single most widely used result in quantum mechanics. The factor of $\frac{2\pi}{\hbar}$ depends on the choice of perturbing potential, but the $|V_{n1}|^2 g(E_m)$ term appears for any applied perturbation. Be careful about the density of energy states - one sometimes encounters density of frequency states (which differs by a factor of $\hbar$) or of wavevector states.

It may appear that need to know the density of final states, $g(E_m)$, but this is not always true. In cases where $|V_{mk}| = 0$ transitions are forbidden, and in some cases we can deduce $g(E_m)$ from the relative rates of related transitions.

5.6 Example of Golden rule - beta decay

A nucleus decays via the reaction n → p e$^-$ $\overline{\nu}$. to form a electron and antineutrino, releasing energy E_0.

The simplest form for the matrix element describing nuclear β-decay is given by the so-called Fermi ansatz $V_{mk} = G_F M/\Omega$ where Ω is the normalisation volume for the wavefunctions, $|M|^2 \approx 1$ is the wavefunction overlap between initial and final nuclear states and G_F is a constant.

We can work in the COM reference frame, so the kinetic energy of the nucleus is zero. Momentum is conserved, so the final state has nuclear, electron and neutrino momentum $\mathbf{P} + \mathbf{p} + \mathbf{q}$=0 while the energy released goes into the electron and neutrino, which for simplicity we treat as massless: $E_0 = E_e + qc$ The proton and neutron are heavy compared with the electron and neutrino. Given that momentum must be conserved, the kinetic energy must be concentrated in the lighter particles.

The density of final states for the electron is given by the phase space volume

$$dn = \frac{d^3\mathbf{p} d^3\mathbf{r}}{(2\pi\hbar)^3}$$

with a similar expression for the neutrino. Number of states in a volume of phase space is given by the number of electron states, times the number of neutrino states, provided energy is conserved:

$$dn = \frac{d^3\mathbf{p} d^3\mathbf{r}}{(2\pi\hbar)^3} \frac{d^3\mathbf{q} d^3\mathbf{r}}{(2\pi\hbar)^3} \delta(E_e + qc - E_0)$$

Using the relativistic relation $E^2 = p^2c^2 + m^2c^4$ implies $\quad \dfrac{dp}{dE} = \dfrac{E}{pc^2}$

the normalisation volume is just $\int d^3\mathbf{r} = \Omega$, and rotational invariance gives $d^3\mathbf{p} = 4\pi p^2 dp$.

All of which which simplifies the integral to

$$dn = \frac{\Omega^2}{4\pi^4\hbar^6c^6} E_e \sqrt{E_e^2 - m_e^2c^4}\, E_\nu^2 \delta(E_e + E_\nu - E_0) dE_e dE_\nu$$

where E_e is the electron energy and E_ν is the neutrino energy. What can actually be measured is the electron energy, so we integrate over the neutrino energies,

$$\frac{dn}{dE_e} = \frac{\Omega^2}{4\pi^4\hbar^6c^6} E_e \sqrt{E_e^2 - m_e^2c^4} (E_0 - E_e)^2$$

This is the distribution of electron energies from beta decay: the rate fo emission of electrons at a particular energy is given by the Golden Rule

$$R = \frac{2\pi}{\hbar} \frac{G_F^2 M^2}{4\pi^4\hbar^6c^6} E_e \sqrt{E_e^2 - m_e^2c^4} (E_0 - E_e)^2$$

Figure shows the simplest case of beta-emission: neutron decay. Conservation laws tell us that the electron energy must lie between its rest mass (0.51MeV) and the total energy available (0.7823MeV). But the entire shape can be deduced from geometry.