Fermi's golden rule

Let $\Psi(x,t)$ be the following linear combination of the first two eigenstates of an infinite square well potential.

$$\Psi(x,t) = c_1(t)\psi_1(x)\exp(-i\omega_1 t) + c_2(t)\psi_2(x)\exp(-i\omega_2 t)$$

Given the perturbing potential

$$V(x,t) = \left(x - \frac{L}{4}\right)^2 \sin(\omega t)$$

we want to solve for $c_2(t)$ and find the transition rate

$$\frac{d}{dt}|c_2(t)|^2$$

From the time-dependent Schrodinger equation we have

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = \hat{H}(x)\Psi(x,t) + V(x,t)\Psi(x,t)$$

The left-hand side works out to be

$$\begin{aligned} LHS = \left(i\hbar\frac{\partial c_1(t)}{\partial t} + \hbar\omega_1 c_1(t)\right)\psi_1(x)\exp(-i\omega_1 t) \\ + \left(i\hbar\frac{\partial c_2(t)}{\partial t} + \hbar\omega_2 c_2(t)\right)\psi_2(x)\exp(-i\omega_2 t) \end{aligned}$$

Using the time-independent Schrodinger equation the right-hand side is

$$RHS = c_1(t)E_1\psi_1(x)\exp(-i\omega_1 t) + c_2(t)E_2\psi_2(x)\exp(-i\omega_2 t) + V(x,t)\Psi(x,t)$$

The energy terms cancel by the substitutions $E_1 = \hbar\omega_1$ and $E_2 = \hbar\omega_2$ leaving

$$\begin{aligned} LHS &= i\hbar\frac{\partial c_1(t)}{\partial t}\psi_1(x)\exp(-i\omega_1 t) + i\hbar\frac{\partial c_2(t)}{\partial t}\psi_2(x)\exp(-i\omega_2 t) \\ RHS &= V(x,t)\Psi(x,t) \end{aligned}$$

Hence

$$i\hbar\frac{\partial c_1(t)}{\partial t}\psi_1(x)\exp(-i\omega_1 t) + i\hbar\frac{\partial c_2(t)}{\partial t}\psi_2(x)\exp(-i\omega_2 t) = V(x,t)\Psi(x,t)$$

Take the inner product of $\psi_2^*(x)$ with the above equation to obtain

$$i\hbar\frac{\partial c_2(t)}{\partial t}\exp(-i\omega_2 t) = c_1(t)M_{21}\sin(\omega t)\exp(-i\omega_1 t) + c_2(t)M_{22}\sin(\omega t)\exp(-i\omega_2 t)$$

where M_{21} and M_{22} are the matrix elements

$$M_{21} = \int \psi_2^*(x) \left(x - \frac{L}{4}\right)^2 \psi_1(x)\, dx$$
$$M_{22} = \int \psi_2^*(x) \left(x - \frac{L}{4}\right)^2 \psi_2(x)\, dx$$

Cancel exponentials.

$$i\hbar \frac{\partial c_2(t)}{\partial t} = c_1(t) M_{21} \sin(\omega t) \exp\bigl(i(\omega_2 - \omega_1)t\bigr) + c_2(t) M_{22} \sin(\omega t)$$

The initial state is $\Psi(x,0) = \psi_1(x)$ hence the initial conditions are

$$c_1(0) = 1, \quad c_2(0) = 0$$

Then for time t near the origin we can use the approximation

$$i\hbar \frac{\partial c_2(t)}{\partial t} = M_{21} \sin(\omega t) \exp\bigl(i(\omega_2 - \omega_1)t\bigr)$$

Solve for $c_2(t)$ by integrating.

$$c_2(t) = \frac{M_{21}}{i\hbar} \int_0^t \sin(\omega t') \exp\bigl(i(\omega_2 - \omega_1)t'\bigr)\, dt'$$

The solution is

$$c_2(t) = \frac{M_{21}}{2i\hbar} \left(\frac{\exp\bigl(i(\omega_2 - \omega_1 - \omega)t\bigr) - 1}{\omega_2 - \omega_1 - \omega} - \frac{\exp\bigl(i(\omega_2 - \omega_1 + \omega)t\bigr) - 1}{\omega_2 - \omega_1 + \omega} \right) \tag{1}$$

For perturbations such that $\omega \approx \omega_2 - \omega_1$ the first term dominates so discard the second term and write

$$c_2(t) = \frac{M_{21}}{2i\hbar} \left(\frac{\exp\bigl(i(\omega_2 - \omega_1 - \omega)t\bigr) - 1}{\omega_2 - \omega_1 - \omega} \right)$$

Rewrite as

$$c_2(t) = \frac{M_{21}}{2\hbar}\, t \exp\left(i\, \frac{\omega_2 - \omega_1 - \omega}{2}\, t\right) \operatorname{sinc}\left(\frac{\omega_2 - \omega_1 - \omega}{2}\, t\right) \tag{2}$$

The probability density is

$$|c_2(t)|^2 = \frac{|M_{21}|^2}{4\hbar^2}\, t^2 \operatorname{sinc}^2\left(\frac{\omega_2 - \omega_1 - \omega}{2}\, t\right)$$

Use the following approximation for sinc^2

$$\mathrm{sinc}^2\left(\frac{\omega_2-\omega_1-\omega}{2}\,t\right) \approx \frac{2\pi}{t}\delta(\omega_2-\omega_1-\omega), \quad t>0$$

to obtain

$$|c_2(t)|^2 = \frac{\pi}{2\hbar^2}|M_{21}|^2 t\delta(\omega_2-\omega_1-\omega) \tag{3}$$

Differentiate $|c_2(t)|^2$ with respect to t to obtain the transition rate.

$$\frac{d}{dt}|c_2(t)|^2 = \frac{\pi}{2\hbar^2}|M_{21}|^2\delta(\omega_2-\omega_1-\omega)$$

For the infinite square well it can be shown that

$$M_{21} = \int_0^L \psi_2^*(x)\left(x-\frac{L}{4}\right)^2\psi_1(x)\,dx = -\frac{8L^2}{9\pi^2} \tag{4}$$

Hence the transition rate is

$$\frac{d}{dt}|c_2(t)|^2 = \frac{32L^4}{81\pi^3\hbar^2}\,\delta(\omega_2-\omega_1-\omega)$$