Fermi's Golden Rule

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We start with the formula of time-dependent perturbation theory,

$$\langle \psi_f | \, \psi \rangle = \delta_{fi} - \frac{i}{\hbar} \int_0^t \langle \phi_f | \, H'(t') \, | \phi_i \rangle \;\; e^{i\omega_{fi}t'} \; dt'$$

Assume $H'(t)$ is a constant in time so that $H'(t) = H'$ and assume the initial and final states are different so that $\delta_{fi} = 0$. Define $H'_{fi} \equiv \langle \phi_f | \, H' \, | \phi_i \rangle$ and $E_{fi} \equiv \hbar\omega_{fi}$.

$$\langle \psi_f | \, \psi \rangle = -\frac{i}{\hbar} H'_{fi} \int_0^t e^{i\omega_{fi}t'} \; dt' = -\frac{i}{\hbar} H'_{fi} \left[\frac{1}{i\omega_{fi}} e^{i\omega_{fi}t'} \right]_o^t$$

$$= -\frac{H'_{fi}}{\hbar\omega_{fi}} (e^{i\omega_{fi}t} - 1) = \frac{H'_{fi}}{E_{fi}} (1 - e^{i\omega_{fi}t})$$

The probability that the system will be in a specific state $|\phi_f\rangle$ at time t is

$$P_{fi}(t) = | \, \langle \psi_f | \, \psi \rangle \, |^2 = \frac{|H'_{fi}|^2}{E_{fi}^2} (1 - e^{-i\omega_{fi}t})(1 - e^{i\omega_{fi}t})$$

$$= \frac{|H'_{fi}|^2}{E_{fi}^2} (2 - 2\cos(\omega_{fi}t)) = 4 \frac{|H'_{fi}|^2}{E_{fi}^2} \sin^2 \left(\frac{E_{fi}t}{2\hbar} \right)$$

The probability that the system will be in any state other than the initial state at time t is given by integrating over all possible final state energies and weighting with the density of states $\rho(E_f)$

$$P_{*i}(t) = \int_0^\infty P_{fi}(t) \rho(E_f) \; dE_f = 4|H'_{fi}|^2 \int_0^\infty \frac{1}{E_{fi}^2} \sin^2 \left(\frac{E_{fi}t}{2\hbar} \right) \rho(E_f) \; dE_f$$

In this expression we can see the effects of the Heisenberg uncertainty principle. In fact, the parameter of the sine function is demonstrating the time-energy uncertainty principle. As time increases, the sine function will oscillate more rapidly with changes in E_f, which will cause cancellation in the integral. To eliminate the effects of the uncertainty principle, we can look at the limit of large time. We use the following representation of the Dirac delta function

$$\delta(x) = \lim_{a \to \infty} \frac{1}{\pi} \frac{\sin^2(ax)}{ax^2}$$

Then the probability that the system will be in any state other than the initial state after a long time is

$$P_{*i}^\infty = \lim_{t \to \infty} P_{*i}(t) = \lim_{t \to \infty} 4|H'_{fi}|^2 \int_0^\infty \frac{\pi t}{2\hbar} \delta(E_{fi}) \rho(E_f) \; dE_f$$

$$= \lim_{t \to \infty} \frac{2\pi t}{\hbar} |H'_{fi}|^2 \int_0^\infty \rho(E_f) \delta(E_f - E_i) \; dE_f$$

The transition rate Γ is the probability per unit time. After the system experiences the constant perturbation for a long time, the transition rate for the system to transition to any state other than the initial state becomes the constant

$$\Gamma_{*i} = \frac{dP_{*i}^\infty}{dt} = \frac{2\pi}{\hbar} |H'_{fi}|^2 \int_0^\infty \rho(E_f) \delta(E_f - E_i) \; dE_f$$

This is Fermi's second golden rule. Notice that the delta function ensures that the system can only transition to states with the same energy as the initial state.