Time-Dependent Perturbations and Fermi's Golden Rule
A (Hopefully) Tantalizing Overview

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Consider a quantum system (atom, spins etc.) under the influence of a Hamiltonian $\hat{H}_0$ perturbed by a (possibly time-dependent) perturbation $\hat{V}$: $\hat{H}(t) = \hat{H}_0 + \hat{V}$. Under the effect of the perturbation, the system "jumps" between two eigenstates $|i(t)\rangle$ and $|f(t)\rangle$ of the unperturbed Hamiltonian.

Note that the subscripts i and f meaning, respectively, "initial" and "final", are not defined with respect to time flow but simply as different dynamical states of the system, which can evolve separately as $|i(0)\rangle \to |i(t)\rangle = e^{-i\,E_i^{(0)}t/\hbar}\,|i(0)\rangle$ and $|f(0)\rangle \to |f(t)\rangle = e^{-i\,E_f^{(0)}t/\hbar}\,|f(0)\rangle$.

If the perturbation is explicitly time-dependent i.e. $\hat{V}(t) = \hat{A}\,f(t)$, the amplitude for the system undergoing the transition is, **to first order in** V:

$$\begin{aligned} c_f(t) &= \delta_{fi} - \frac{i}{h}\int_0^t dt'\, e^{i\left(E_f^{(0)} - E_i^{(0)}\right)t'/\hbar}\ \langle f(t')|\,\hat{V}(t')\,|i(t')\rangle \\ &\equiv \delta_{fi} - \frac{i}{h}\int_0^t dt'\, e^{i\,\omega_{fi}\,t'}\ V_{fi}(t'), \end{aligned} \tag{1}$$

where $\omega_{fi} \equiv \left(E_f^{(0)} - E_i^{(0)}\right)/\hbar \equiv E_{fi}/\hbar$ is the transition frequency.

Note the effect of the Kronecker delta:

- if $f = i$, then
$$c_f(t) = 1 - \frac{i}{h}\int_0^t dt'\ V_{ii}(t')$$
- if $f \neq i$, then
$$c_f(t) = -\frac{i}{h}\int_0^t dt' e^{i\,\omega_{fi}\,t'}\ V_{fi}(t')$$

The $i \to f$ transition probability is (for $i \neq f$):

$$\mathcal{P}_{if}(t) = |c_f(t)|^2 = \frac{1}{\hbar^2}\ |\,\langle f(t)|\,\hat{A}\,|i(t)\rangle\,|^2\ |F(\omega_{fi}, t)|^2\ , \tag{2}$$

where $F(\omega_{fi}, t) = \int_0^t dt' \, f(t') \, \exp(i \, \omega_{fi} \, t')$. A transition probability rate Γ_{if} can be obtained by taking the time derivative of Eq.(2). Depending on the form of $f(t)$, this rate may or may not be time-dependent. Some authors call this Fermi's Golden Rule (or simply the Golden Rule, since it was actually Dirac who first pointed out its utility). To get a feel for the implications of Eq. (2), consider an elastically bound charge in a transient uniform electric field) or a spin-1/2 charged particle in a time-dependent magnetic field (magnetic resonance).

Nevertheless, the **real** power of FGR is associated with perturbations that are either oscillatory (e.g. atom–light interactions) or time-independent (e.g. scattering). For harmonic perturbations ($\hat{V} = \hat{V}_0 \, e^{\pm i \omega t}$), FGR becomes:

$$\Gamma_{if} \equiv \frac{d\mathcal{P}_{if}}{dt} = \frac{2\pi}{\hbar} \, | \langle f | \, \hat{V} \, | i \rangle \, |^2 \;\; \delta \left(E_f^{(0)} - E_i^{(0)} \pm \hbar \, \omega \right) , \tag{3}$$

which can be generalized to

$$\Gamma_{if} \equiv \frac{d\mathcal{P}_{if}}{dt} = \frac{2\pi}{\hbar} \, | \langle f | \, \hat{V} \, | i \rangle \, |^2 \;\; \delta \left(E_f^{(0)} - E_i^{(0)} \pm E \right) . \tag{4}$$

The most striking feature of Eqs. (3, 4) is that the energy levels ($E_{i,f}^{(0)}$) involved in the transition are *infinitely sharp*—a quite restrictive requirement. In many cases, processes such as Doppler or collision broadening cause transitions to occur from an energy level to an energy *band* (or *continuum*), characterized by a spread in energy ($E_f, E_f + dE_f$) or momentum ($\mathbf{k}_f, \mathbf{k}_f + d\mathbf{k}_f$). In this case, the "barebones" expressions (3, 4) must be summed over all the energies (or momenta) in the continuum. The net outcome is that Eqs. (3, 4) now define an *infinitesimal* transition rate (i.e. $\Gamma_{if} \to d\Gamma_{if}$), whereby the Dirac delta function—the condition of resonant absorption/emission between $E_{i,f}^{(0)}$—is replaced by the distribution of modes per unit energy interval, i.e. the energy density $\rho(E) d\Omega$:

$$d\Gamma_{if} = \frac{2\pi}{\hbar} \, | \langle f | \, \hat{V} \, | i \rangle \, |^2 \;\; \rho(E) d\Omega$$

hence

$$\Gamma_{if} = \int d\Gamma_{if} = \int \frac{2\pi}{\hbar} \;\; | \langle f | \, \hat{V} \, | i \rangle \, |^2 \;\; \rho(E) d\Omega \tag{5}$$

Eq. (5) can be summed, if needed, over various other degrees of freedom involved (e.g. spin states, polarization directions etc.). The density of states can be expressed in terms of the energy spectrum as follows:

- in momentum (wavenumber) space,

$$\rho(E) d\Omega = \frac{V}{(2\pi)^3} \, k^2 \, \left(\frac{dk}{dE} \right) \, d\Omega,$$

- in frequency space,

$$\rho(E)d\Omega = \frac{V}{(2\pi c)^3}\,\omega^2\,\left(\frac{d\omega}{dE}\right)\,d\Omega.$$

If the transition involves a single—for now non-quantized—photon of energy $E = \hbar\omega = \hbar kc$ (as in Eq. 3), the density of states is:

$$\rho(E)d\Omega \equiv \rho(\omega)d\Omega = \frac{V}{\hbar(2\pi c)^3}\,\omega^2\,d\Omega.$$

We will cover applications of FGR explicitly when we study light-atom interactions: spontaneous/ stimulated emission, stimulated absorption, blackbody radiation.