5 Time-dependent Perturbation Theory I

Consider time-dependent perturbation in Hamiltonian

$$H = H_0 + \hat{V}(t) \tag{1}$$

with H_0 constant in time and exactly soluble as before, $H_0|n\rangle = E_n|n\rangle$, $\langle n|n'\rangle = \delta_{nn'}$. Recall H_0 time-ind. $\Longrightarrow$ time evolution of soln to $i\hbar\partial|\psi\rangle/\partial t = H_0|\psi\rangle$ is $|\psi(t)\rangle = \Sigma_n c_n|n\rangle \exp(-i\hbar E_n t/\hbar)$. With full t-dependent H, write solution with time-dependent coefficients

$$|\psi(t)\rangle = \sum_n c_n(t)e^{-i\hbar E_n t/\hbar}|n\rangle \tag{2}$$

and plug in:

$$\begin{aligned}(H_0 + \hat{V}(t))|\psi\rangle &= i\hbar\frac{\partial|\psi\rangle}{\partial t} \qquad (3)\\ \sum_n \left(E_n + \hat{V}\right) c_n(t)e^{-i\hbar E_n t/\hbar}|n\rangle &= \sum_n \left(i\hbar\frac{dc_n}{dt} + E_n c_n(t)\right) e^{-i\hbar E_n t/\hbar}|n\rangle\end{aligned}$$

Inner product with $\langle m|$:

$$i\hbar\frac{dc_m}{dt} = \sum_n \langle m|\hat{V}(t)|n\rangle c_n(t)e^{i(E_m - E_n)t/\hbar}, \tag{4}$$

i.e. set of coupled diff. eq. for $c_m(t)$.

Perturbation turned on at t=0

Large class of interesting problems can be defined by assuming system evolves according to H_0 until $t = 0$, at which time perturbation $\hat{V}(t)$ is turned on. Assume system is in eigenstate $|n\rangle$ at $t = 0$, then initial conditions are

$$c_m(t = 0) = \delta_{m,n} \tag{5}$$

Now look at $t > 0$ but very small, such that still have $c_n \simeq 1$ and $c_m \ll c_n, \quad m \neq n$. Then can drop all terms except $m = n$ on rhs of (4), find

$$i\hbar \frac{dc_m}{dt} = \langle m|\hat{V}(t)|n\rangle e^{i(E_m - E_n)t/\hbar}, \tag{6}$$

which can be directly integrated:

$$\boxed{c_m \simeq \tfrac{1}{i\hbar}\int_0^t dt' \langle m|\hat{V}(t')|n\rangle e^{i(E_m-E_n)t'/\hbar}, \quad m \neq n} \tag{7}$$

5.1 Transition probabilities

Can derive some quite general 1st order results for transition probabilities which go under name of Fermi golden rule–useful for calculations in wide variety of physical situations, back-of-envelope estimates!

1st consider situation when perturbation is oscillatory:

$$\hat{V}(t) = \hat{V}_0 \cos\omega t \tag{8}$$

& we want to consider transitions induced between two eigenstates $|i\rangle$ and $|f\rangle$ of H_0, i.e. at $t = 0$ state is $|i\rangle$.[1] Plugging into (7) and using $\cos\omega t = (e^{i\omega t} + e^{-i\omega t})/2$, and[2]

$$\hbar\omega_0 \equiv E_f - E_i, \tag{9}$$

find after performing t-integral

$$c_f(t) = -\frac{1}{2\hbar}\langle f|\hat{V}_0|i\rangle \left[\frac{e^{i(\omega_0+\omega)t} - 1}{\omega_0 + \omega} + \frac{e^{i(\omega_0-\omega)t} - 1}{\omega_0 - \omega}\right] \tag{10}$$

If $\omega \simeq \omega_0$ the external frequency nearly matches the energy of the transition, so we can neglect the 1st term,[3] giving

$$c_f(t) \simeq -\frac{1}{2\hbar}\langle f|\hat{V}_0|i\rangle \frac{e^{i(\omega_0-\omega)t} - 1}{\omega_0 - \omega} \tag{11}$$

Probability atom is in state $|f\rangle$ at time t is $|c_f(t)|^2$. Using identity $|e^{i\theta} - 1|^2 = 2(1-\cos\theta) = 4\sin^2\theta/2$, find

[1] We will neglect coupling to other states, so formally we are solving the *two-level system*.

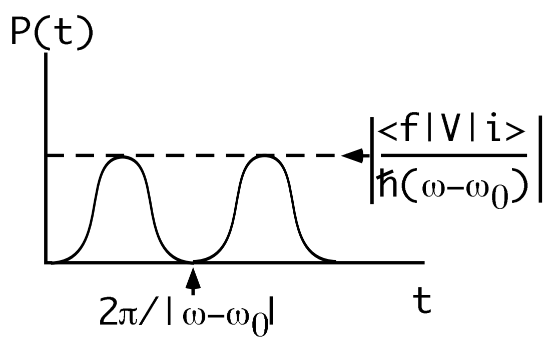
[2] Note $\hbar\omega_0 > 0$ means atom has absorbed photon, $\hbar\omega_0 < 0$ that atom has emitted photon.

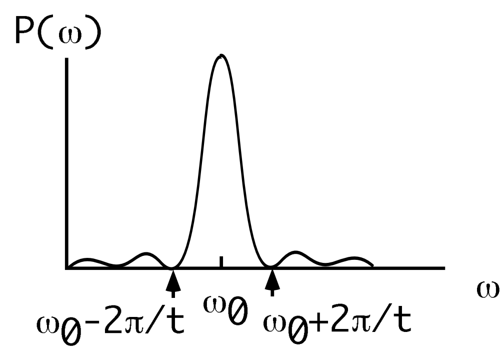
[3] One has to be a little careful about this argument, in the sense that we are assuming that we can make ω sufficiently close to ω_0 such that the 2nd term becomes arbitrarily large with respect to the first. Still, for fixed t and $V(t)$, we must remember that we can't have $c_f(t) > 1$. We are assuming that the time can be chosen sufficiently small such that our perturbation expansion still works, even arbitrarily close to ω_0.

$$\boxed{P_f = \frac{|\langle f|\hat{V}_0|i\rangle|^2}{\hbar^2}\frac{\sin^2[(\omega-\omega_0)t/2]}{(\omega-\omega_0)^2}} \tag{12}$$

What does this mean? Strangely, it means that the probability of making a transition is actually oscillating sinusoidally (squared)! If you want to cause a transition, should turn off perturbation after time $\pi/|\omega_0-\omega|$ or some odd multiple, when the system is in upper state with maximumu probability.

As fctn. of frequency, P_f peaked at $\omega=\omega_0$. Central peak has height $|V_{fi}t/2\hbar|^2$ and *width* $4\pi/t$, getting higher and narrower as time goes on (see fig.) Recall this is perturbative treatment, however: can't get bigger than 1, so perturbation theory breaks down eventually.





5.2 Stimulated radiative transition in H hyperfine structure

Want to see if we can cause a transition between levels with a "photon", which we describe at this stage by a classical electromagnetic wave. For simplicity we consider 1st the hyperfine-split ground state, i.e. the transition between triplet and singlet leading to the 21 cm "line". The magnetic field is 1st treated classically as propagating wave:

$$\mathbf{B} = B_0\vec{\epsilon}\cos\omega t \tag{13}$$

where $\vec{\epsilon}$ is the polarization vector and ω the angular frequency of the radiation. We'll take $\epsilon = \hat{x}$ first, so perturbation is [4]

$$\hat{V} = -\mu \cdot \mathbf{B} = g\frac{e}{2mc}B_0\ \hat{S}^e_x \cos\omega t \tag{14}$$

Now we can use our formalism: final state $\langle f|$ is the singlet $\langle 0,0|$, initial state triplet $|i\rangle = |1M\rangle$.

$$\langle f|\hat{V}|i\rangle = \frac{ge}{2mc}B_0\cos\omega t\langle 0,0|\hat{S}^e_x|1M\rangle \tag{15}$$

$$= \frac{geB_0\cos\omega t}{2mc}\left(\frac{\langle\uparrow\downarrow|-\langle\downarrow\uparrow|}{\sqrt{2}}\right)\left(\frac{\hat{S}^e_+ + \hat{S}^e_-}{2}\right)\begin{cases}|\uparrow\uparrow\rangle\\ \frac{|\uparrow\downarrow\rangle+|\downarrow\uparrow\rangle}{\sqrt{2}}\\ |\downarrow\downarrow\rangle\end{cases} \tag{16}$$

$$= \frac{ge\hbar B_0\cos\omega t}{2mc}\left(\frac{\langle\uparrow\downarrow|-\langle\downarrow\uparrow|}{\sqrt{2}}\right)\begin{cases}|\downarrow\uparrow\rangle/2\\ \frac{|\uparrow\uparrow\rangle+|\downarrow\downarrow\rangle}{2\sqrt{2}}\\ |\uparrow\downarrow\rangle/2\end{cases} \tag{17}$$

$$= \frac{ge\hbar B_0\cos\omega t}{4\sqrt{2}mc}\begin{cases}-1\\ 0\\ 1\end{cases} \tag{18}$$

Note there is no matrix element for a transition to $M = 0$ for this polarization[5]. The coefficient c_f becomes ($M = \pm 1$)

$$c_f = \mp\frac{1}{2i\hbar}\frac{g_eB_0}{4\sqrt{2}mc}\int_0^t dt'\ \underbrace{e^{-i\omega_0 t}}_{\hbar\omega_0 = E_f - E_i}\underbrace{\left(\frac{e^{i\omega t}+e^{-i\omega t}}{2}\right)}_{=\cos\omega t} \tag{19, 20}$$

This is same integral we had to do before, with same result (since overall sign of c_f doesn't affect P_f)

$$P = \frac{g^2e^2B_0^2}{32m^2c^2\hbar^2}\frac{\sin^2(\omega-\omega_0)t/2}{(\omega-\omega_0)^2} \quad (\vec{\epsilon} \parallel \hat{x}) \tag{21}$$

[4] Q1: Why have we neglected the electric field, which is after all part of the travelling wave? The question becomes more puzzling if you estimate the magnitudes of the perturbations of the electric and magnetic effects on a charge confined to an orbit of size a_0: the magnetic effects are a factor of α=1/137 times smaller! A1: Point is only magnetic field couples to *spin*, and therefore only $\hat{V}_{Magnetic}$ can cause transitions between the hyperfine states (see below). Q2: Why is it only the electron spin that couples to magnetic field? A2: The proton spin couples too, but since it comes with a magnetic moment $g_pe/2m_pc$, it's about 2000 times smaller, so we neglect it.

[5] This is a special case of a so-called "selection rule", in which all matrix elements for a given perturbation V vanish except for a few "select" ones characterized by special changes in the quantum numbers

Angular dependence for linear polarization

Hyperfine radiation has characteristic *polarization dependence*. Suppose $\vec{\epsilon}$ is in x-z plane for simplicity, $\mathbf{S}\cdot\vec{\epsilon} = \hat{S}^e_x \sin\theta + \hat{S}^e_z \cos\theta$. Redo previous calculation, noting that $\hat{S}^e_z$ has no nonzero matrix elements with $\langle f|$ and $|i\rangle$, since both $\langle f|$ and $|i\rangle$ are eigenstates of $\hat{S}_z$ and $\langle f|i\rangle = 0$. So only contribution is $\hat{S}_x$ component, which now enters with add'l factor $\sin^2\theta$.

$$P = \frac{g^2 e^2 B_0^2}{32 m^2 c^2} \frac{\sin^2(\omega-\omega_0)t/2}{(\omega-\omega_0)^2} \sin^2\theta \quad (\vec{\epsilon} = \sin\theta\hat{x} + \cos\theta\hat{z}) \tag{22}$$

Physical interpretation of $P \longrightarrow 0$ when $\theta \longrightarrow 0$: if $\mathbf{B} \parallel \hat{z}$, system invariant under rotations about $\hat{z} \Longrightarrow \hat{L}_z$ is conserved. So transitions with $M = \pm 1$ are not allowed.

Circular polarization

Now shine circularly polarized light on H-atom.,

$$\mathbf{B} = B_0(\hat{i}\cos\omega t + \hat{j}\sin\omega t) \tag{23}$$

i.e. $\mathbf{B}$ rotates in x-y plane w/ angular freq. ω. In addition to matrix elts of $\hat{S}_x$ and $\hat{S}_z$ which we've calculated, we'll need

$$\begin{aligned}
\langle f|\hat{S}_y|i\rangle &= \langle 0,0|\hat{S}^e_y|1M\rangle && (24)\\
&= \left(\tfrac{\langle\uparrow\downarrow| - \langle\downarrow\uparrow|}{\sqrt{2}}\right)\left(\tfrac{\hat{S}^e_+ - \hat{S}^e_-}{2i}\right)\begin{cases} |\uparrow\uparrow\rangle \\ \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}} \\ |\downarrow\downarrow\rangle \end{cases} && (25)\\
&= -\tfrac{i\hbar}{2}\left(\tfrac{\langle\uparrow\downarrow| - \langle\downarrow\uparrow|}{\sqrt{2}}\right)\begin{cases} -|\downarrow\uparrow\rangle \\ \frac{|\uparrow\uparrow\rangle - |\downarrow\downarrow\rangle}{\sqrt{2}} \\ |\uparrow\downarrow\rangle \end{cases} && (26)\\
&= \tfrac{\hbar}{2\sqrt{2}}\begin{cases} -i \\ 0 \\ -i \end{cases} && (27)
\end{aligned}$$

So for $M = \pm 1$, prob. ampl. is (recall $\hbar\omega_0 \equiv E_f - E_i < 0$ for the emission process we're calculating here!):

$$\begin{aligned} c_f &= \frac{1}{i\hbar}\int_0^t dt' \langle f|\hat{V}|i\rangle e^{i\omega_0 t'}, \text{ where} \\ \langle f|\hat{V}|i\rangle &= \frac{geB_0}{2mc}\left(\langle f|\hat{S}_x|i\rangle \cos\omega t' + \langle f|\hat{S}_y|i\rangle \sin\omega t'\right) \\ &= \frac{geB_0}{2mc} \cdot \frac{-M\hbar}{2\sqrt{2}} \cdot (\cos\omega t' + iM \sin\omega t') \end{aligned} \tag{28}$$

and we find

$$c_f = \frac{iM}{4\sqrt{2}}\,\frac{geB_0}{2mc}\int_0^t dt' e^{i(\omega_0 + M\omega)t'}. \tag{29}$$

Now the exponent in (29) can be small only if $\omega_0 + M\omega \simeq 0$, or $M = +1$, since $\omega_0 < 0$, take $\omega > 0$ always. For this case we get large transition amplitude. But if $M = -1$, exponent is large and integrand oscillates rapidly $\Longrightarrow$ $c_f \to 0$. *"photon" interpretation*: circularly polarized light has angular momentum z-component $M = +1$ if propagation is along $\hat{z}$ and phases are chosen as in (23). Angular momentum conservation means that atom initially in state $M = +1$, finally in state $M = 0$, outgoing photon has $M = +1$, consistent with general conservation law

$$M_i = M_f + M_{photon} \quad \text{(emission)} \tag{30}$$

and we have deduced that M_{photon} is $+1$ for right- and -1 for left-circularly polarized radiation.[6] We could redo the argument for an *absorption process*, and find

$$M_i + M_{photon} = M_f \quad \text{(absorption)} \tag{31}$$

[6] In this naive treatment of the electromagnetic field, there is no difference between the argument for stimulated and sponatneous emission. It is easiest to think of spontaneous emission, where the outgoing photon has $M_{photon} = +1$, as stated. But the calculation also applies to stimulated emission, where now M_{photon} has to be thought of as the difference in the z-components of the photon field in the final state (2 photons) minus the initial state (1 photon). So a process where the incoming photon has $M = -1$, but the outgoing photons have both M=0, during which process the atom makes the transition from $M = +1$ to $M = 0$ is also possible. See sec. 5.3.

5.3 Einstein argument relating absorption, stimulated & spontaneous emission

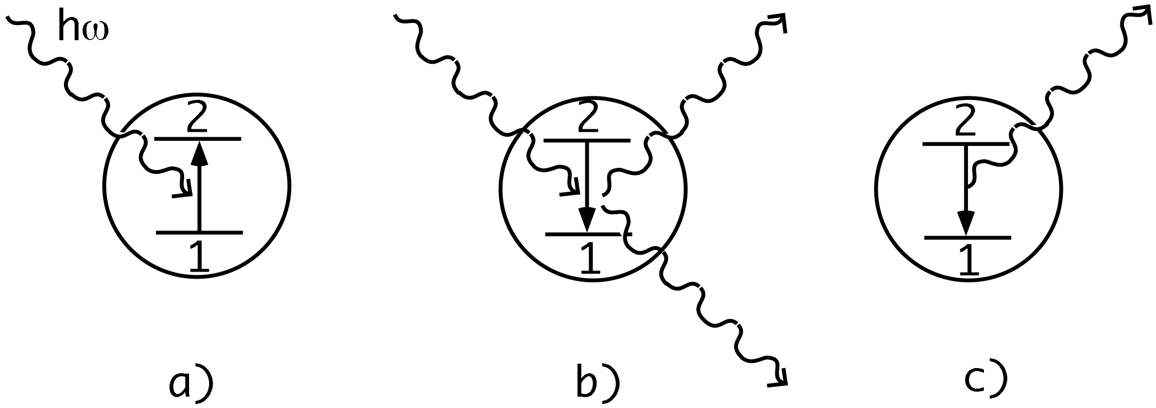


Figure 1: Three types of emission processes: a) absorption; b) stimulated emission; and c) spontaneous emission

The calculations we have done for 2-level systems so far makes it plausible that an externally applied electromagnetic field can cause transitions between states, and we have seen there is a possible crude interpretation in terms of "photons" even at this ("first-quantized") level. But the simplest process one is taught about in, e.g. chemistry classes is in some sense the hardest to understand. Why does atom in excited state emit light spontaneously? A single excited atom sitting in empty space has an *infinite* lifetime based on the quantum mechanics we have learned so far, because, the excited state is an eigenstate of the Hamiltonian! How can it decay, emitting light?

Answer is actually beyond scope of course. What we think of as "vacuum" is in quantum electrodynamics a very active medium, continually being "polarized" by quantum fluctuations, i.e. particle-antiparticle pairs which live for a short time (short enough to satisfy Heisenberg's uncertainty principle $\Delta E \Delta t \simeq \hbar$) and then decay. These processes can, in analogy to an externally applied classical field (stimulated emission), cause transitions in nearby atoms. Another way to think of it is to put an atom in a large box. The Hamiltonian now has to be solved together with the modes of the box, and the eigenstates of H_0 are no longer eigenstates of the full system–hence they decay.

How can we say anything about spontaneous emission and its relation to the other processes if we can't calculate it within the same framework? We may do so thanks to an elegant statistical argument by Einstein.

Recall treatment of blackbody radiation–box of volume V with periodic B.C.

$$\mathbf{B} = \mathbf{B_0}\hat{\epsilon}_{\mathbf{k}} \cos(\mathbf{k} \cdot \mathbf{r} - \omega t), \tag{32}$$

where $\hat{\epsilon}_{\mathbf{k}}$ is unit vector representing polarization of $\mathbf{B}$ field for mode $\mathbf{k}$. Note there are 2 linearly ind. polarization vectors $\perp \mathbf{k}$.

Periodicity:

$$k_x V^{1/3} = 2\pi n_x, \text{with } n_x \text{ integer, etc.} \tag{33}$$

so number of modes in d^3k is

$$\begin{aligned} d^3n &= 2dn_x dn_y dn_z \quad \text{(2 polarizations)} \\ &= \frac{2V}{(2\pi)^3} d^3k. \end{aligned} \tag{34}$$

Now make analogy with classical physics. Must be that in total radiation field we have energy density

$$\mathcal{E} = \frac{E^2 + B^2}{8\pi} \tag{35}$$

so energy in a given mode is

$$\underbrace{n}_{\text{no. photons/mode}} \hbar\omega = \frac{B_0^2}{8\pi} \cdot \underbrace{\frac{1}{2}}_{\text{mean of } \cos^2} \cdot \underbrace{2}_{E^2+B^2=2B^2} \cdot V \tag{36}$$

$$\text{so} \qquad n = \frac{B_0^2 V}{8\pi\hbar\omega} \text{ photons.} \tag{37}$$

Now do statistics: prob. for n photons to be excited at temp. T is

$$P_n = \frac{e^{-n\hbar\omega/k_BT}}{\sum_n e^{-n\hbar\omega/k_BT}} \tag{38}$$

– leads to Bose-Einstein distribution– avg. number of photons in equilibrium at temp. T is

$$\langle n\rangle = \sum_n nP_n = \frac{1}{e^{\hbar\omega/k_BT} - 1} \tag{39}$$

Now add some atoms to the mix: N_1 in ground state, N_2 in excited state $\hbar\omega$ above grnd. state. In equilibrium,

$$\frac{N_2}{N_1} = e^{-\hbar\omega/k_BT} \tag{40}$$

Now consider detailed balance of radiation field and atoms which can absorb at energy $\hbar\omega_0$, as well as undergo stimulated emission with energy $\hbar\omega_0$.

Absorption rate *Rate* of absorption of photons by atoms in ground state must be prop. to # of photons to absorb and number of atoms around to absorb them:

$$\left.\frac{dN_1}{dt}\right|_{abs} = -CN_1n = -\frac{CN_1}{e^{\hbar\omega_0/k_BT} - 1} \tag{41}$$

Stimulated rate must be proportional to the number of atoms in the excited state at any time. Therefore put

$$\left.\frac{dN_1}{dt}\right|_{stim} = BnN_2 = Bn(N_1e^{-\hbar\omega_0/k_BT}) \tag{42}$$

$$= \frac{BN_1e^{-\hbar\omega_0/k_BT}}{e^{\hbar\omega_0/k_BT} - 1} \tag{43}$$

Spontaneous emission This happens independent of the number of photons present, so

$$\left.\frac{dN_1}{dt}\right|_{spon} = AN_2 = AN_1e^{-\hbar\omega_0/k_BT} \tag{44}$$

Number conservation for atoms in ground state (in equilibrium!):

$$\left.\frac{dN_1}{dt}\right|_{abs} + \left.\frac{dN_1}{dt}\right|_{spon} + \left.\frac{dN_1}{dt}\right|_{stim} = 0 \tag{45}$$

$$\text{so} \quad C = A(1 - e^{-\hbar\omega_0/k_B T}) + Be^{-\hbar\omega_0/k_B T} \tag{46}$$

Now draw several consequences from simple result:

1. As $T \to \infty$, $e^{-\hbar\omega_0/k_B T} \to 1$ so we learn that $B = C$, *rate per atom of stimulated emission equal to rate of absorption.* This is the same result we derived from microscopic theory for a single atomic transition. [7]

2. Insert into (46) to find $B = A$ as well, so there's only one overall const.

3. Summarize: If rate of absorption from given mode is nN_1A, spontaneous decay rate is N_2A, stimulated rate is nN_2A, and the net (sum of stimulated & spontaneous) decay rate *to* mode is $N_2(1+n)A$.

5.4 Continuum of final states: Fermi Golden Rule

$\star$ Note this whole calculation has been done thinking only about atoms interacting with monochromatic radiation, ang. freq. ω_0. If we put atoms in a cavity at some temperature T, would expect a *distribution* of frequencies, e.g. blackbody. Let's be more general and ask what happens if the radiation field has some distribution of frequencies to which the atoms might decay, characterized by a density of states (no. states/ energy interval) $\rho(\omega)$.

So to get probability for transition due to one of the modes, integrate over final states assuming that probabilities for transitions from different modes add independently (*incoherent perturbations*):

$$P_f = \frac{|\langle f|\hat{V}_0|i\rangle|^2}{\hbar^2} \int_{-\infty}^{\infty} d\omega\ \rho(\omega) \frac{\sin^2[(\omega-\omega_0)t/2]}{(\omega-\omega_0)^2} \tag{47}$$

[7] Be amazed: Einstein was able to derive this result in a statistical fashion knowing almost zero about quantum theory! At the time, absorption and spontaneous emission had classical counterparts (think of the decay of an orbiting charged particle in a classical atom), but stimulated emission was a new idea. Einstein showed there was no detailed balance unless these processes were included.

Suppose now that the peak of $\sin^2[(\omega - \omega_0)t/2]/(\omega - \omega_0)^2$ is much narrower than the spread of frequencies in ρ_0. Then allowed to approximate $\rho(\omega)$ by $\rho(\omega_0)$. Integral may now be made dimensionless and performed, $\int_{-\infty}^{\infty} dx\ \sin^2(x/2)/x^2 = \pi/2$, so we get

$$P_f \simeq \frac{\pi|\langle f|\hat{V}_0|i\rangle|^2}{2\hbar^2}\rho(\omega_0)t \tag{48}$$

P_f is the probability of a transition, so the rate of making transitions is

$$\boxed{R_f = \frac{dP_f}{dt} \simeq \frac{P_f}{t} = \frac{\pi|\langle f|\hat{V}_0|i\rangle|^2}{2\hbar^2}\rho(\omega_0)} \tag{49}$$

This is one version of the *Fermi golden rule*.