Time Dependent Perturbation Theory (Weider, pg. 204).

We now consider the time evolution of a perturbed system, keeping $\hat{V}$, for the time being, independent of time. We need a general expression for the time evolution operator $\hat{U}(t, t_0)$:

time indep. potential. $\rightarrow$ $$\hat{U}(t, t_0) = \exp\left(-\frac{i}{\hbar}\hat{\mathcal{H}}(t-t_0)\right)$$

as a solution to $\mathcal{H}|\beta\rangle = i\hbar\frac{d}{dt}|\beta\rangle$

[This is not the general expression for $\hat{U}$, including a time dependent $\hat{V}$. The general expression is an integral equ., as we shall see below.

$$\hat{U}(t, t_0) = 1 - \frac{i}{\hbar}\int_{t_0}^{t} \hat{\mathcal{H}}(\tau)\hat{U}(\tau, t_0)\,d\tau$$
]

What would be nice is to express $\hat{U}(t, t_0)$ in terms of a perturbation expansion in $\hat{U}^0(t, t_0)$, where

$$\hat{U}^0(t, t_0) = \exp\left[-\frac{i}{\hbar}\hat{\mathcal{H}}_0(t-t_0)\right].$$

But since $\hat{\mathcal{H}}$ & $\hat{V}$ do not necessarily commute, then

$$e^{\hat{\mathcal{H}}+\hat{V}} \neq e^{\hat{\mathcal{H}}}e^{\hat{V}}.$$

For small λ, we can write a (convergent) series expansion

$$\hat{U}(t, t_0) = \hat{U}^{(0)}(t, t_0) + \sum_{n=1}^{\infty}\hat{U}^{(n)}(t, t_0)$$

Ordering is important!

$$\hat{U}^{(n)} = \left(\frac{-i\lambda}{\hbar}\right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1$$
$$\times\, \hat{U}^{(0)}(t, \tau_n)\hat{V}(\tau_n)\hat{U}^{(0)}(\tau_n, \tau_{n-1})\cdots\hat{U}^{(0)}(\tau_2, \tau_1)\hat{V}(\tau_1)\hat{U}^{0}(\tau_1, t_0)$$

If V is independent of time, then $\hat{U}(t, t_0)$ is a function of $\Delta t = t - t_0$ only.

Suppose we start with a system in a particular eigenstate $|\varepsilon_i^{(0)}\rangle$ at $t_0 = 0$:

$$\Rightarrow \underbrace{|\beta_i, t\rangle}_{\text{state at time } t} = \hat{U}(t)|\varepsilon_i^{(0)}\rangle .$$

The probability of observing the system in another state of $\hat{\mathcal{H}}^0$ at some later time t is then

$$\mathcal{P}_{ij}(t) = |\langle \varepsilon_j^{(0)} | \beta_i\, t\rangle|^2 = |\langle \varepsilon_j^{(0)} | \hat{U}(t) | \varepsilon_i^{(0)}\rangle|^2$$

For processes such as scattering etc, we are interested in long time (asymptotic) processes and we define a transition rate between states as

trans. rate $= R_{ij} = \lim_{t\to\infty} \frac{d\mathcal{P}_{ij}(t)}{dt} = \lim_{t\to\infty} \frac{d}{dt} |\underline{\langle \varepsilon_j^{(0)} | \hat{U}(t) | \varepsilon_i^{(0)}\rangle}|^2$

expand this in the power series form to give

$$R_{ij} = \lim_{t\to\infty} \frac{d}{dt} \left| \langle \varepsilon_j^{(0)} | U^{(0)} | \varepsilon_i^{(0)}\rangle + \langle \varepsilon_j^{(0)} | \sum_{n=1}^{\infty} U^{(n)} | \varepsilon_i^{(0)}\rangle \right|^2$$

The first term goes like δ_{ij} since $U|\varepsilon_i^{(0)}\rangle \rightarrow e^{i(\text{phase})}|\varepsilon_i^{(0)}\rangle$

$$\Rightarrow R_{ij} = \lim_{t\to\infty} \frac{d}{dt} \left| \sum_{n=1}^{\infty} \langle \varepsilon_j^{(0)} | U^{(n)} | \varepsilon_i^{(0)}\rangle \right|^2 .$$

(Note that $R \propto \sum_n \lambda^n$, implying that $R \rightarrow 0$ as $\lambda \rightarrow 0$, as expected)

Now, let's work to first order in λ only, and use a time independent V:

$$R_{ij} = \lim_{t\to\infty} \frac{d}{dt} \left| \langle \epsilon_j^{(0)} | \hat{U}^{(1)}(t) | \epsilon_i^{(0)} \rangle \right|^2$$

Where
$$U^{(1)}(t) = -\frac{i\lambda}{\hbar} \int_0^t d\tau_1 \, \hat{U}^0(t,\tau_1) \cdot \hat{V} \cdot \hat{U}^{(0)}(\tau_1, 0)$$
$$= -\frac{i\lambda}{\hbar} \int_0^t d\tau_1 \, e^{-\frac{i}{\hbar}\hat{\mathcal{H}}_0 (t-\tau_1)} \cdot \hat{V} \cdot e^{-\frac{i}{\hbar}\hat{\mathcal{H}}_0 (\tau_1)}$$

$$\Rightarrow R_{ij} = \lim_{t\to\infty} \frac{d}{dt} \left| \langle \epsilon_j^{(0)} | \left(-\frac{i\lambda}{\hbar}\right) \int_0^t d\tau_1 \, e^{-\frac{i}{\hbar}\hat{\mathcal{H}}_0 (t-\tau_1)} \hat{V} e^{-\frac{i}{\hbar}\hat{\mathcal{H}}_0 (\tau_1)} | \epsilon_i^{(0)} \rangle \right|^2$$
$$= \frac{\lambda^2}{\hbar^2} \lim_{t\to\infty} \frac{d}{dt} \left| \langle \epsilon_j^{(0)} | \int d\tau_1 \, e^{-\frac{i}{\hbar}\epsilon_j^{(0)}(t-\tau_1)} \hat{V} e^{-\frac{i}{\hbar}\epsilon_i^{(0)}\tau_1} | \epsilon_i^{(0)} \rangle \right|^2$$

(pull all τ_1 terms out)
$$= \frac{\lambda^2}{\hbar^2} \lim_{t\to\infty} \frac{d}{dt} \left| \underbrace{e^{-\frac{i}{\hbar}\epsilon_j^{(0)} t}}_{\text{This is just a phase, removed by complex square.}} \langle \epsilon_j^{(0)} | \hat{V} | \epsilon_i^{(0)} \rangle \int d\tau_1 \, e^{\frac{i}{\hbar}(\epsilon_j^{(0)} - \epsilon_i^{(0)})\tau_1} \right|^2$$

$$= \frac{\lambda^2}{\hbar^2} |V_{ji}|^2 \lim_{t\to\infty} \frac{d}{dt} \left| \int_0^t d\tau_1 \, e^{\frac{i}{\hbar}(\epsilon_j^{(0)} - \epsilon_i^{(0)})\tau_1} \right|^2$$

Define $\omega = \frac{\epsilon_j^{(0)} - \epsilon_i^{(0)}}{\hbar}$ then the integral becomes

$$\left| \frac{1}{\omega} \int_0^{\omega t} d\xi \, e^{i\xi} \right|^2 = \frac{1}{\omega^2} \left| -i \int_0^{i\omega t} dz \, e^z \right|^2$$
$$= \frac{1}{\omega^2} \left| e^{i\omega t} - 1 \right|^2 \quad (-i \text{ has been removed})$$
$$= \frac{1}{\omega^2} \left(1 - e^{i\omega t} - e^{-i\omega t} + 1 \right)$$
$$= 2(1 - \cos\omega t)/\omega^2$$

$$\therefore R_{ij} = \frac{\lambda^2}{\hbar^2} |V_{ji}|^2 \lim_{t\to\infty} \frac{d}{dt} \left(\frac{2(1-\cos\omega t)}{\omega^2} \right)$$

(3-4) Now, $2\frac{(1-\cos\omega t)}{\omega^2}$ has two arguments, ω & t. We call it $F(\omega,t)$

want to find an asymptotic expression for it as $t \to \infty$

We take this function and define an associated one

$$\frac{1}{t}F(\omega,t) = \frac{1}{t} \times \frac{2(1-\cos\omega t)}{\omega^2} \longrightarrow \frac{1}{t}\frac{2\left(1-\left(1-\frac{(\omega t)^2}{2}\right)\right)}{\omega^2}$$

(1) $\to t$ as $\omega \to 0$.

$\therefore$ as $t \to \infty$, the peak value goes to ∞ as well, the peak being at $\omega = 0$.

(2) The integral under the peak is

$$\int_{-\infty}^{\infty} \frac{2(1-\cos\omega t)}{t\,\omega^2}\,d\omega = \int_{-\infty}^{\infty}\frac{2(1-\cos\xi)}{\xi^2}\,d\xi = 4\int_0^{\infty}\frac{1-\cos\xi}{\xi^2}\,d\xi = 2\pi$$

$$\int_0^{\infty}\frac{1-\cos\xi}{\xi^2}\,d\xi = \int_0^{\infty}\frac{1-(-\sin^2\frac{\xi}{2}+\cos^2\frac{\xi}{2})}{\xi^2}\,d\xi$$

$$= \int_0^{\infty}\frac{1+\sin^2\xi/2-\cos^2\xi/2}{\xi^2}\,d\xi = 2\int_0^{\infty}\frac{\sin^2\frac{\xi}{2}}{\xi^2}\,d\xi = \int_0^{\infty}\frac{\sin^2 x}{x^2}\,dx$$

Use $\int_0^{\infty}\frac{\sin^2 x}{x^2}\,dx = \frac{\pi}{2} \Rightarrow \int\frac{F(\omega,t)}{t}\,d\omega = 4\cdot\frac{\pi}{2} = 2\pi$.

These two properties are just what one expects for a delta function. $\therefore$ we identify $2\frac{(1-\cos\omega t)}{\omega^2} \to 2\pi t\,\delta(\omega)$

so the area comes out properly

$$\Rightarrow \quad R_{ji} = \frac{\lambda^2}{\hbar^2}|V_{ji}|^2 \lim_{t\to\infty}\frac{d}{dt}\left[2\pi t\,\delta(\omega_{ji})\right]$$

So $R_{ji} = \frac{2\pi\lambda^2}{\hbar^2}\left|V_{ji}\right|^2\delta(\omega_{ji})$ ← [Fermi's Golden Rule. 1st order perturbation Thy]

Now, this shows that transitions are only allowable between states of the same energy.

Transitions Induced by a Harmonic Perturbation

Suppose now that $\hat{V}$ is time dependent, of the form

$$\lambda\hat{V} = \lambda\hat{V}(\hat{r})\cos\omega t = \lambda\hat{V}(\hat{r})\underbrace{\tfrac{1}{2}\left(e^{i\omega t}+e^{-i\omega t}\right)}_{\cos\omega t}.$$

This represents a plane of polarization of, for example, a radiation field.

Then the same expression can be used as before except now V is time dependent.

$$\text{So, } R_{ij} = \frac{\lambda^2}{\hbar^2}\lim_{t\to\infty}\frac{d}{dt}\left|\langle\epsilon_j^{(0)}|\int d\tau_1\, e^{-\frac{i}{\hbar}\epsilon_j^{(0)}(t-\tau_1)}\hat{V}(r) \times\tfrac{1}{2}\left(e^{i\omega\tau_1}+e^{-i\omega\tau_1}\right)e^{-\frac{i}{\hbar}\epsilon_i^{(0)}\tau_1}|\epsilon_i^{(0)}\rangle\right|^2$$

$$= \frac{\lambda^2}{\hbar^2}|V_{ji}|^2\lim_{t\to\infty}\frac{d}{dt}\left|\tfrac{1}{2}\int e^{\frac{i}{\hbar}(\epsilon_j^{(0)}-\epsilon_i^{0}-\hbar\omega)\tau_1}d\tau_1 + \tfrac{1}{2}\int e^{\frac{i}{\hbar}(\epsilon_j^{(0)}-\epsilon_i^{(0)}+\hbar\omega)\tau_1}d\tau_1\right|^2$$

$$= \frac{2\pi\lambda^2}{\hbar}|V_{ji}|^2\,\tfrac{1}{2}\left[\delta(\omega_{ji}-\omega)+\delta(\omega_{ji}+\omega)\right].$$

($\leftarrow$ why isn't this 1/4? See page 8-8)

Unlike the time independent case, we now have

$$\omega_{ji} = \pm\omega$$

i.e. transitions can now occur between states with different energies. One process is induced emission while the other is induced absorption.

Finally, since $|V_{ij}|^2 = |V_{ji}|^2$, both the absorption and emission rates can be written as $R_{ij} = \frac{2\pi\lambda^2}{2\hbar^2}|V_{ij}|^2\left[\delta(\omega_{ij}-\omega)+\delta(\omega_{ij}+\omega)\right]$.

Radiative transitions in Hydrogen

As an application, we consider what happens to hydrogen atoms in a black-body radiation background. The interaction is similar to the Stark Effect:

$$\vec{E} = \underline{\underline{\vec{E}_0}} \cos \omega t$$

assume that this is constant over the dimensions of the atom. OK for visible light; poor for x-rays.

$$\Rightarrow \lambda \hat{V} = e\vec{E} \cdot \vec{r} = e\vec{E}_0 \cdot \vec{r} \cos \omega t .$$

$$R_{ij} = \frac{2\pi e^2}{\hbar^2} \frac{1}{2} \left| \vec{E}_0 \langle i | \vec{r} | j \rangle \right|^2 \left(\delta(\omega_{ij} + \omega) + \delta(\omega_{ij} - \omega) \right) .$$

Now, $\vec{E}_0$ is a function of ω in the black body example; that is, there is a distribution of intensities as a function of ω.

$$\therefore \underline{\underline{\int R_{ij}\, d\omega}} = \frac{2\pi e^2}{2\hbar^2} \left| \vec{E}_0(\omega_{ij}) \cdot \langle i | \vec{r} | j \rangle \right|^2 .$$

Probability for emission etc. for ω between ω and $\omega + d\omega$

Further, there are three planes of polarization, which are randomly oriented and therefore we have to average over 3.

$$\therefore \int R_{ij}\, d\omega = \frac{\pi e^2}{\hbar^2} \frac{1}{3} \left\{ |E_0(\omega_{ij}) \langle i | x | j \rangle |^2 + x \leftrightarrow y + x \leftrightarrow z \right\}$$

$$= \frac{\pi e^2}{\hbar^2} \frac{E_0^2(\omega_{ij})}{3} \left| \langle i | \vec{r} | j \rangle \right|^2 .$$

The strength of the transitions clearly depends on two things:

i) the magnitude of $\mathcal{E}^2$, which is proportional to the radiation energy density $\rho_{rad} = |\mathcal{E}|^2/4\pi$

ii) the magnitude of the matrix element $\langle i|\vec{r}|j\rangle$. This leads to selection rules for the transitions, both in terms of which states i & j are connected, and which planes of polarization are active.

For example, let's look at hydrogen interacting with light plane polarized along the z-axis.

$$z_{ij} = \int \psi^*_{n'\ell' m_\ell'} \, r\cos\theta \, \psi_{n\ell m_\ell} \, d\mathbf{r}$$

$$= \int R^*_{n'\ell'} R_{n\ell} \, r^3 dr \underbrace{\int_{-1}^{1} P^*_{\ell' m_\ell'}(u) P_{\ell m_\ell}(u)\, u \, du}_{} \underbrace{\int_0^{2\pi} e^{-i(m_\ell' - m_\ell)\phi} d\phi}_{}$$

This gives 0 unless $\ell' = \ell \pm 1$
{follows from using
$P_{\ell m} = \frac{1}{u}\left[\frac{\ell - m + 1}{2\ell+1} P_{\ell+1,m} + \left(\frac{\ell+m}{2\ell+1}\right) P_{\ell-1,m}\right]$

This give 0 unless $m_\ell = m_\ell'$
[could also include spin $\delta_{m_s m_s'}$].

There are many other subtleties involving black body distributions etc, into which we will not go. See texts for a discussion of Einstein coeffs.

From 8-5

Aside: To get the form of R_{ij} in the harmonic perturbation example, we use the following:

Define $\omega_\pm = \omega_{ji} \pm \omega$ $\qquad \omega_{ji} = (\epsilon_j^{(0)} - \epsilon_i^{(0)})/\hbar$.

Then
$$\left| \frac{1}{2} \int e^{\frac{i}{\hbar}(\epsilon_j^{(0)} - \epsilon_i^{(0)} - \omega\hbar)\tau} d\tau + \frac{1}{2} \int e^{\frac{i}{\hbar}(\epsilon_j^{(0)} - \epsilon_i^{(0)} + \omega\hbar)\tau} d\tau \right|^2$$

$$= \frac{1}{4} \left| \frac{1}{\omega_-}(e^{i\omega_-\tau} - 1) + \frac{1}{\omega_+}(e^{i\omega_+\tau} - 1) \right|^2$$

Assume that the $\frac{1}{\omega}$ factors work out. $\rightarrow$
$$= \frac{1}{4} \left| (e^{-i\omega_-\tau} + e^{-i\omega_+\tau} - 2)(e^{i\omega_-\tau} + e^{i\omega_+\tau} - 2) \right|^2$$

$$= \frac{1}{4} \left(1 + e^{i(\omega_+ - \omega_-)\tau} - 2e^{-i\omega_-\tau} + e^{-i(\omega_+ - \omega_-)\tau} + 1 - 2e^{-i\omega_+\tau} - 2e^{i\omega_-\tau} - 2e^{i\omega_+\tau} + 4 \right)$$

$$= \frac{1}{4} \left(\underbrace{-2 + 4}_{+2} - 2(e^{i\omega_+\tau} + e^{-i\omega_+\tau}) + 4 - 2(e^{i\omega_-\tau} + e^{-i\omega_-\tau}) + (e^{i(\omega_+ - \omega_-)\tau} + e^{-i(\omega_+ - \omega_-)\tau}) \right)$$

$$= \frac{1}{4} \left(4 - 2(2\cos\omega_+\tau) + 4 - 2(2\cos\omega_-\tau) + (2\cos(\omega_+ - \omega_-)\tau - 2) \right)$$

$$= \frac{1}{2} \cdot 2 \cdot (1 - \cos\omega_+\tau) + \frac{1}{2} \cdot 2 \cdot (1 - \cos\omega_-\tau) - \frac{1}{2}(1 - \cos(\omega_+ - \omega_-)\tau)$$

$\downarrow$ $\frac{1}{2}\delta(\omega_+)$ $\qquad$ $\downarrow$ $\frac{1}{2}\delta(\omega_-)$ $\qquad$ $\downarrow$ $\frac{1}{4}\delta(2\omega)$

This vanishes.