FERMI'S GOLDEN RULE

We have calculated the probability of observing the system in a state $|k\rangle$ after applying a perturbation to $|\ell\rangle$. Often we are interested in transition probability not to an individual eigenstate, but a distribution of eigenstates. Often the set of eigenstates form a continuum of accepting states, for instance, vibrational relaxation or ionization.

Transfer to a set of continuum (or bath) states forms the basis for a describing irreversible relaxation. Qualitatively, you expect deterministic, oscillatory feedback between discrete quantum states. However, the amplitude of one discrete state coupled to a continuum will decay due to destructive interferences between the oscillating frequencies for each member of the continuum.

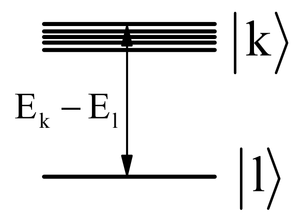
So we are interested in calculating transition probability to a distribution of final states: $\overline{P_k}$.

$P_k = |b_k|^2$ Probability of observing amplitude in discrete eigenstate of H_0

$\rho(E_k)$: Density of states—units in $\left(1/E_k \right)$, describes distribution of final states—all eigenstates of H_0

If we start in a state $|\ell\rangle$, the total transition probability is a sum of probabilities $\overline{P_k} = \sum_k P_k$. We are just interested in the rate of leaving $|\ell\rangle$ and occupying any state $|k\rangle$. or for a continuous distribution:

$$\overline{P}_k = \int dE_k \; \rho(E_k) \, P_k$$

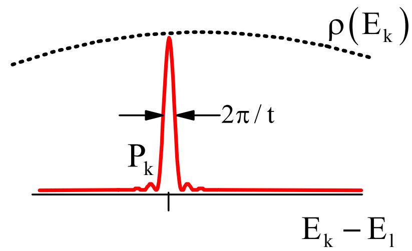


For a constant perturbation:

$$\overline{P}_k = \int dE_k \; \rho(E_k) \, 4 |V_{k\ell}|^2 \, \frac{\sin^2\left((E_k - E_\ell) t / 2\hbar \right)}{|E_k - E_\ell|^2}$$

<u>Let's make two assumptions</u>:

1) $\rho(E_k)$ doesn't vary much with frequency. There are many final states: continuous. Also, t is relatively long.



2) The matrix element $V_{k\ell}$ is invariant across the final states.

These assumptions allow those variables to be factored out of integral

$$\overline{P_k} = \rho(E_k)|V_{k\ell}|^2 \int_{-\infty}^{+\infty} dE_k \; 4\,\frac{\sin^2(E_k - E_\ell)t/2\hbar}{(E_k - E_\ell)^2}$$

We have chosen the limits $-\infty \to +\infty$ since $\rho(E_k)$ is broad relative to P_k. Using

$\int_{-\infty}^{+\infty} d\Delta \frac{\sin^2 a\Delta}{\Delta^2} = a\pi$, with $a = t/\hbar$

$$\overline{P_k} = \frac{2\pi}{\hbar}\rho(E_k)|V_{k\ell}|^2\, t$$

The total transition probability is linearly proportional to time. Often, for instance in relaxation processes, we will be concerned with the transition <u>rate</u>, $\overline{w}_{k\ell}$:

$$\overline{w}_{k\ell} = \frac{\partial \overline{P}_{k\ell}}{\partial t}$$

$$\overline{w}_{k\ell} = \frac{2\pi}{\hbar}\rho(E_k)|V_{k\ell}|^2$$

This is Fermi's Golden Rule. Note rates independent of time. It is very common for chemical rate processes: matrix element squared + D.O.S.

Remember that P_k is centered sharply at $E_k = E_\ell$. So we may write $\rho(E_k = E_\ell)$ or more commonly in terms of $\delta(E_k - E_\ell)$:

$$\bar{w}_{k\ell} = \frac{2\pi}{\hbar}\rho\left(E_k = E_\ell\right)\left|V_{k\ell}\right|^2$$

$$w_{k\ell} = \frac{2\pi}{\hbar}\left|V_{k\ell}\right|^2 \delta\left(E_k - E_\ell\right) \qquad \bar{w}_{k\ell} = \int dE_k\, \rho\left(E_k\right) w_{k\ell}$$

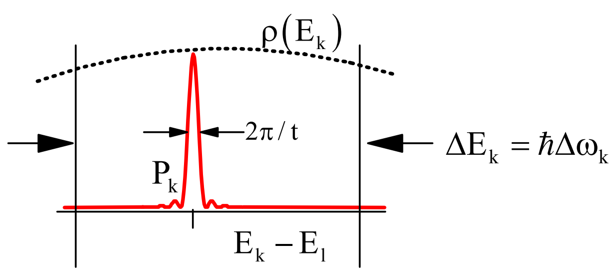
Range of validity:

For discrete states we saw: $\left|V_{k\ell}\right| << \hbar\omega_{k\ell}$

Also P_k never varies much from initial values.

$$P_k = \bar{w}_{k\ell}\left(t - t_0\right) \qquad t << \frac{1}{\bar{w}_{k\ell}}$$

However, transition probability must be sharp compared to $\rho(E_k)$.



$$t >> \hbar / \Delta E_k$$

$$\Delta E >> \bar{w}_{k\ell}\,\hbar$$

$$\Delta\omega_k >> \bar{w}_{k\ell}$$

Golden Rule Rate for Harmonic Perturbations

If we want to calculate the transition rate to a continuum of final states induced by harmonic perturbation, we follow derivation of F.G.R. from before.

Only absorption: $$P_k = \frac{\left|V_{k\ell}{}^2\right|}{4\hbar^2} \frac{\sin^2\left[\left(\omega_{k\ell} - \omega\right)t/2\right]}{\left[\left(\omega_{k\ell} - \omega\right)/2\right]^2}$$

$$\overline{P}_k = \int dE_k \, \rho\left(E_k\right) P_k$$

$$= \int d\omega_k \, \rho\left(\omega_k\right) P_k$$

$$= \frac{\pi}{2\hbar^2} \left|V_{k\ell}\right|^2 \rho\left(\omega_k = \omega_\ell + \omega\right)\left(t\right)$$

$$\overline{w}_{k\ell} = \frac{\partial \overline{P}_k}{\partial t} = \frac{\pi}{2\hbar^2} \left|V_{k\ell}\right|^2 \rho\left(\omega_k = \omega_\ell + \omega\right)$$

$$= \frac{\pi}{2\hbar^2} \left|V_{k\ell}\right|^2 \rho\left(\omega_{k\ell} = \omega\right)$$

or more commonly:

$$w_{k\ell} = \frac{\pi}{2\hbar^2} \left|V_{k\ell}\right|^2 \delta\left(\omega_{k\ell} - \omega\right)$$

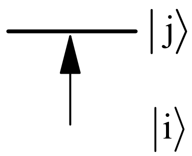
If we include both the absorption and stimulated emission and neglect interferences (i.e., long times):

$$w_{k\ell} = \frac{\pi}{2\hbar^2} \left|V_{k\ell}\right|^2 \left[\delta\left(\omega_{k\ell} - \omega\right) + \delta\left(\omega_{k\ell} + \omega\right)\right]$$

$$= \frac{\pi}{2\hbar} \left|V_{k\ell}\right|^2 \left[\underline{\delta\left(E_k - E_\ell - \hbar\omega\right)} + \underline{\delta\left(E_k - E_\ell + \hbar\omega\right)}\right]$$

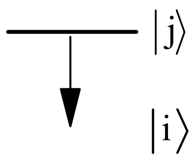
abs: $E_k = E_\ell + \hbar\omega$ S.E. $E_k = E_\ell - \hbar\omega$

Let's look at this expression for the two sets of states $\{|i\rangle\}$ and $\{|j\rangle\}$ where $\varepsilon_j > \varepsilon_i$:



STIMULATED EMISSION

$$\overline{w}_{ij} = \frac{\pi}{2\hbar^2}\left|V_{ij}\right|\rho\left(E_i\right)$$



ABSORPTION

$$\overline{w}_{ji} = \frac{\pi}{2\hbar^2}\left|V_{ji}\right|^2\rho\left(E_j\right)$$

since $\left|V_{ij}\right|^2 = \left|V_{ji}\right|^2$

$$\frac{\overline{w}_{ij}}{\overline{w}_{ji}} = \frac{\rho\left(E_i\right)}{\rho\left(E_j\right)} \qquad \text{detailed balance}$$

The ratio of the rates upward and downward is given by the ratio of the density of states of the photons in the electric field. (More commonly this is seen written for matter in the form that relates the rates for discrete states to the thermal occupation of those states: $w_{ij} / w_{ji} = \exp\left(-\beta\hbar\omega_{ij}\right)$.