

2.5 FERMI'S GOLDEN RULE

The transition rate and probability of observing the system in a state $|k\rangle$ after applying a perturbation to $|\ell\rangle$ from the constant first-order perturbation doesn't allow for the feedback between quantum states, so it turns out to be most useful in cases where we are interested just the rate of leaving a state. This question shows up commonly when we calculate the 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. You can think of the material Hamiltonian for our problem being partitioned into two portions, $H = H_S + H_B + V_{SB}(t)$, where you are interested in the loss of amplitude in the H_S states as it leaks into H_B . 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, using the same ideas as before, let's calculate the transition probability from $|\ell\rangle$ to a distribution of final states: \overline{P}_k .

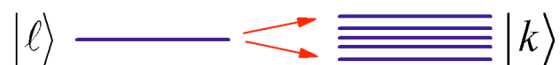
$P_k = |b_k|^2$ Probability of observing amplitude in discrete eigenstate of H_0

$\rho(E_k)$: Density of states—units in $1/E_k$, 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

$$\overline{P}_k = \sum_k P_k. \quad (2.161)$$

We are just interested in the rate of leaving $|\ell\rangle$ and occupying any state $|k\rangle$ or for a continuous distribution:



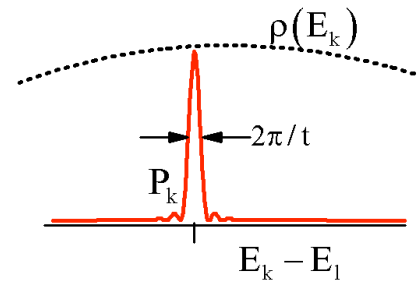
$$\bar{P}_k = \int dE_k \rho(E_k) P_k \quad (2.162)$$

For a constant perturbation:

$$\bar{P}_k = \int dE_k \rho(E_k) 4|V_{k\ell}|^2 \frac{\sin^2\left(\frac{(E_k - E_\ell)t}{2\hbar}\right)}{|E_k - E_\ell|^2} \quad (2.163)$$

Now, let's make two assumptions to evaluate this expression:

- 1) $\rho(E_k)$ varies slowly with frequency and there is a continuum of final states. (By slow what we are saying is that the observation point 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

$$\bar{P}_k = \rho|V_{k\ell}|^2 \int_{-\infty}^{+\infty} dE_k 4 \frac{\sin^2\left(\frac{(E_k - E_\ell)t}{2\hbar}\right)}{(E_k - E_\ell)^2} \quad (2.164)$$

Here, we have chosen the limits $-\infty \rightarrow +\infty$ since $\rho(E_k)$ is broad relative to P_k . Using the identity

$$\int_{-\infty}^{+\infty} d\Delta \frac{\sin^2 a\Delta}{\Delta^2} = a\pi \quad (2.165)$$

with $a = t/\hbar$ we have

$$\bar{P}_k = \frac{2\pi}{\hbar} \rho|V_{k\ell}|^2 t \quad (2.166)$$

The total transition probability is linearly proportional to time. For relaxation processes, we will be concerned with the transition rate, $\bar{w}_{k\ell}$:

$$\bar{w}_{k\ell} = \frac{\partial \bar{P}_{k\ell}}{\partial t} \quad (2.167)$$

$$\bar{w}_{k\ell} = \frac{2\pi}{\hbar} \rho |V_{k\ell}|^2$$

Remember that P_k is centered sharply at $E_k = E_\ell$. So although ρ is a constant, we usually write eq. (2.167) in terms of $\rho(E_k = E_\ell)$ or more commonly in terms of $\delta(E_k - E_\ell)$:

$$\bar{w}_{k\ell} = \frac{2\pi}{\hbar} \rho(E_k = E_\ell) |V_{k\ell}|^2 \quad (2.168)$$

$$w_{k\ell} = \frac{2\pi}{\hbar} |V_{k\ell}|^2 \delta(E_k - E_\ell) \quad \bar{w}_{k\ell} = \int dE_k \rho(E_k) w_{k\ell} \quad (2.169)$$

This expression is known as Fermi's Golden Rule. Note the rates are independent of time. As we will see going forward, this first-order perturbation theory expression involving the matrix element squared and the density of states is very common in the calculation of chemical rate processes.

Range of validity

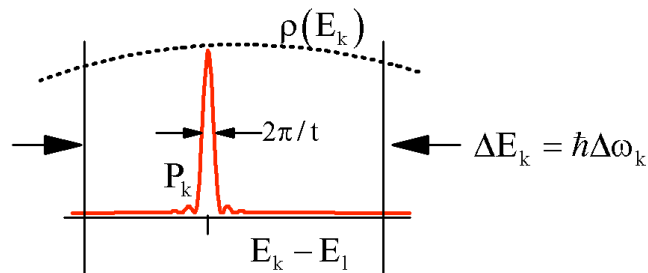
For discrete states we saw that the first order expression held for $|V_{k\ell}| \ll \hbar\omega_{k\ell}$, and for times such that P_k never varies from initial values.

$$P_k = \bar{w}_{k\ell} (t - t_0) \quad t \ll \frac{1}{\bar{w}_{k\ell}} \quad (2.170)$$

However, transition probability must also be sharp compared to $\rho(E_k)$, which implies

$$t \gg \hbar / \Delta E_k \quad (2.171)$$

So, this expression is useful where



$$\Delta E \gg \bar{\omega}_{k\ell} \hbar$$

Andrei Tokmakoff, MIT Department of Chemistry, 2/22/2007

(2.172)

$$\Delta\omega_k \gg \bar{\omega}_{k\ell}$$