PERTURBATION THEORY

Given a Hamiltonian

$$H(t) = H_0 + V(t)$$

where we know the eigenkets for H_0

$$H_0|n\rangle = E_n|n\rangle$$

we often want to calculate changes in the amplitudes of $|n\rangle$ induced by $V(t)$:

$$|\psi(t)\rangle = \sum_n c_n(t)|n\rangle$$

where

$$c_k(t) = \langle k|\psi(t)\rangle = \langle k|U(t,t_0)|\psi(t_0)\rangle$$

In the interaction picture, we defined

$$b_k(t) = \langle k|\psi_I\rangle = e^{+i\omega_k r} c_k(t)$$

which contains all the relevant dynamics. The changes in amplitude can be calculated by solving the coupled differential equations:

$$\frac{\partial}{\partial t} b_k = \frac{-i}{\hbar} \sum_n e^{-i\omega_{nk} t} V_{kn}(t)\, b_n(t)$$

For a complex system or a system with many states to be considered, solving these equations isn't practical.

Alternatively, we can choose to work directly with $U_I(t,t_0)$, and we can calculate $b_k(t)$ as:

$$b_k = \langle k|U_I(t,t_0)|\psi(t_0)\rangle$$

where

$$U_I(t,t_0) = \exp_+\left[\frac{-i}{\hbar}\int_{t_0}^{t} V_I(\tau)\,d\tau\right]$$

Now we can truncate the expansion after a few terms. This is perturbation theory, where the dynamics under H_0 are treated exactly, but the influence of $V(t)$ on b_n is truncated. This works well for small changes in amplitude of the quantum states with small coupling matrix elements relative to the energy splittings involved. $|b_k(t)| \approx |b_k(0)|; |V| \ll |E_k - E_n|$

Transition Probability

Let's take the specific case where we have a system prepared in $|\ell\rangle$, and we want to know the probability of observing the system in $|k\rangle$ at time t, due to $V(t)$.

$$P_k(t) = \left|b_k(t)\right|^2 \qquad\qquad b_k(t) = \langle k | U_I(t,t_0) | \ell \rangle$$

$$b_k(t) = \left\langle k \left| \exp_+\left[-\frac{i}{\hbar}\int_{t_0}^{t} d\tau\, V_I(\tau) \right] \right| \ell \right\rangle$$

$$\begin{aligned} &= \langle k|\ell\rangle \;-\; \frac{i}{\hbar}\int_{t_0}^{t} d\tau \langle k|V_I(\tau)|\ell\rangle \\ &\quad + \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \,\langle k|V_I(\tau_2)V_I(\tau_1)|\ell\rangle \quad + \ldots \end{aligned}$$

using

$$\langle k|V_I(t)|\ell\rangle = \langle k|U_0^\dagger\; V(t)\, U_0|\ell\rangle = e^{-i\omega_{\ell k} t}\; V_{k\ell}(t)$$

$$b_k(t) = \delta_{k\ell} - \frac{i}{\hbar}\int_{t_0}^{t} d\tau_1\; e^{-i\omega_{\ell k}\tau_1} V_{k\ell}(\tau_1) \qquad \text{“first order”}$$

$$+\sum_m \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1\; e^{-i\omega_{mk}\tau_2}\; V_{km}(\tau_2) e^{-i\omega_{\ell m}\tau_1}\; V_{m\ell}(\tau_1) \quad + \ldots \qquad \text{“second order”}$$

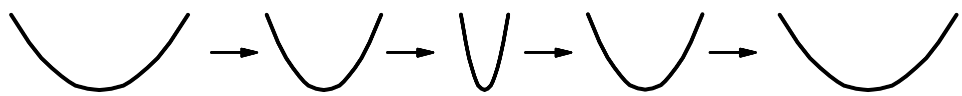
This expression is usually truncated at the appropriate order. Including only the first integral is first-order perturbation theory.

If $|\psi_0\rangle$ is not an eigenstate, we only need to express it as a superposition of eigenstates, but remember to convert to $c_k(t) = e^{-\omega_k t}\; b_k(t)$.

Note that if the system is initially prepared in a state $|\ell\rangle$, and a time-dependent perturbation is turned on and then turned off over the time interval $t = -\infty$ to $+\infty$, then the complex amplitude in the target state $|k\rangle$ is just the Fourier transform of V(t) evaluated at the energy gap $\omega_{\ell k}$.

Example: First-order Perturbation Theory

Vibrational excitation on compression of harmonic oscillator. Let's subject a harmonic oscillator to a Gaussian compression pulse, which increases the frequency of the h.o.



$$H = \frac{p^2}{2m} + k(t)\frac{x^2}{2}$$

$$A' = \delta k_0 = A/\sqrt{2\pi\sigma}$$

$$k(t) = k_0 + \delta k(t) \qquad \delta k(t) = A' \exp\left(-\frac{(t-t_0)^2}{2\sigma^2}\right) \qquad k_0 = m\Omega^2$$

$$H = H_0 + V(t) = \underbrace{\frac{p^2}{2m} + k_0\frac{x^2}{2}}_{H_0} + \underbrace{\frac{A'x^2}{2}\exp\left(-\frac{(t-t_0)^2}{2\sigma^2}\right)}_{V(t)}$$

$$H_0|n\rangle = E_n|n\rangle \qquad H_0 = \hbar\Omega\left(a^\dagger a + \frac{1}{2}\right) \qquad E_n = \hbar\Omega\left(n + \frac{1}{2}\right)$$

If the system is in $|0\rangle$ at $t_0 = -\infty$, what is the probability of finding it in $|n\rangle$ at $t = \infty$?

for $n \neq 0$:

$$b_n(t) = \frac{-i}{\hbar}\int_{t_0}^{t} d\tau\ V_{n0}(\tau)\, e^{i\omega_{n0}\tau}$$

$$= \frac{-i}{\hbar} A' \langle n|x^2|0\rangle \int_{-\infty}^{+\infty} d\tau\ e^{i\omega_{n0}\tau} e^{-\tau^2/2\sigma^2}$$

$\omega_{n0} = n\Omega$

$$b_n(t) = \frac{-i}{\hbar} A' \langle n|x^2|0\rangle \int_{-\infty}^{+\infty} d\tau\ e^{in\Omega\tau - \tau^2/2\sigma^2}$$

$$\int_{-\infty}^{+\infty} \exp\left(ax^2 + bx + c\right) dx = \sqrt{\frac{-\pi}{a}}\,\exp\left(c - \frac{1}{4}\frac{b^2}{a}\right)$$

$$b_n(t) == \frac{-i}{\hbar} A \langle n | x^2 | 0 \rangle \, e^{-2n^2\sigma^2\Omega^2/4}$$

What about matrix element?

$$x^2 = \frac{\hbar}{m\Omega}\left(a + a^\dagger\right)^2 = \frac{\hbar}{m\Omega}\left(aa + a^\dagger a + aa^\dagger + a^\dagger a^\dagger\right)$$

First-order perturbation theory won't allow transitions to $n = 1$, only $n = 0$ and $n = 2$.

Generally this wouldn't be realistic, because you would certainly expect excitation to v=1 would dominate over excitation to v=2. A real system would also be anharmonic, in which case, the leading term in the expansion of the potential V(x), that is linear in x, would not vanish as it does for a harmonic oscillator, and this would lead to matrix elements that raise and lower the excitation by one quantum.

However for the present case,

$$\langle 2 | x^2 | 0 \rangle = \sqrt{2}\,\frac{\hbar}{m\Omega}$$

So,

$$b_2 = \frac{-\sqrt{2}i}{m\Omega} A \, e^{-2\sigma^2\Omega^2}$$

$$P_2 = |b_2|^2 = \frac{2\,A^2}{m^2\Omega^2} e^{-4\sigma^2\Omega^2} \qquad\qquad A = \delta k_0 \sqrt{2\pi\sigma}$$

Significant transfer of amplitude occurs when the compression pulse is short compared to the vibrational period.

$$\frac{1}{\sigma} << \Omega$$

<u>Validity</u>: First order doesn't allow for feedback and b_n can't change much from its initial value.

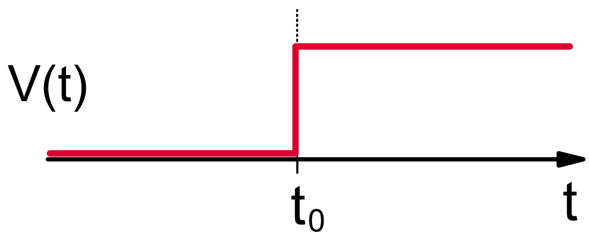
for $P_2 \approx 0 \quad |A| << |m\Omega|$

First-Order Perturbation Theory

A number of important relationships in quantum mechanics that describe rate processes come from 1st order P.T. For that, there are a couple of model problems that we want to work through:

(1) **Constant Perturbation**

$|\psi(t_0)\rangle = |\ell\rangle$. A constant perturbation of amplitude V is applied to t_0. What is P_k?



$$V(t) = \theta(t - t_0)\,V = \begin{cases} 0 & t < 0 \\ V & t \geq 0 \end{cases}$$

To first order, we have:

$$b_k = \delta_{k\ell} - \frac{i}{\hbar}\int_{t_0}^{t} d\tau\; e^{i\omega_{k\ell}(\tau - t_0)} V_{k\ell}$$

$V_{k\ell}$ independent of time

$$\left\langle k \left| U_0^\dagger\, V\, U_0 \right| \ell \right\rangle = V\, e^{i\omega_{k\ell}(t - t_0)}$$

$$= \delta_{k\ell} + \frac{-i}{\hbar} V_{k\ell} \int_{t_0}^{t} d\tau\; e^{i\omega_{k\ell}(\tau - t_0)}$$

$$= \delta_{k\ell} + \frac{-V_{k\ell}}{E_k - E_\ell}\left[\exp\left(i\omega_{k\ell}(t - t_0)\right) - 1\right]$$

using $e^{i\varnothing} - 1 = 2ie^{i\varnothing/2}\sin\varnothing/2$

$$= \delta_{k\ell} + \frac{-2iV_{k\ell}\, e^{i\omega_{k\ell}(t - t_0)/2}}{E_k - E_\ell}\sin\left(\omega_{k\ell}(t - t_0)/2\right)$$

For $k \neq \ell$ we have

$$P_k = \left|b_k\right|^2 = \frac{4\left|V_{k\ell}\right|^2}{\left|E_k - E_\ell\right|^2}\sin^2 \tfrac{1}{2}\omega_{k\ell}(t - t_0)$$

or setting $t_0 = 0$ and writing this as we did in lecture 1:

$$P_k = \frac{V^2}{\Delta^2}\sin^2(\Delta t/\hbar) \qquad \text{where } \Delta = \frac{E_k - E_l}{2}$$

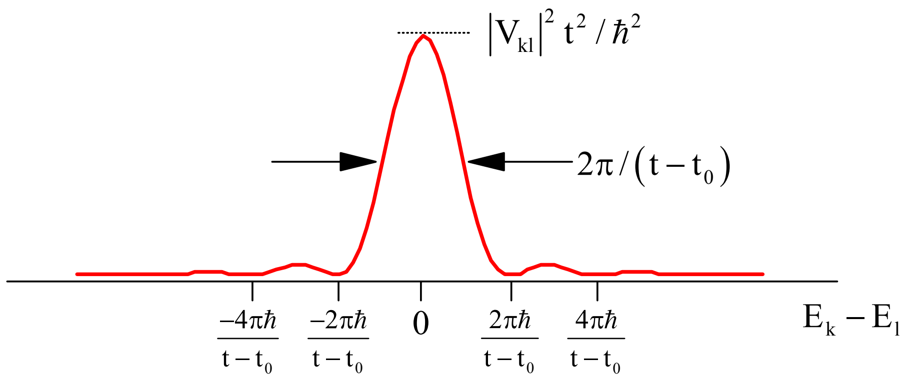
$$\text{or } P_k = \frac{V^2 t^2}{\hbar^2}\text{sinc}^2(\Delta t/2\hbar)$$

Compare this with the exact result:

$$P_k = \frac{V^2}{V^2+\Delta^2}\sin^2\left(\sqrt{\Delta^2+V^2}\,t/\hbar\right)$$

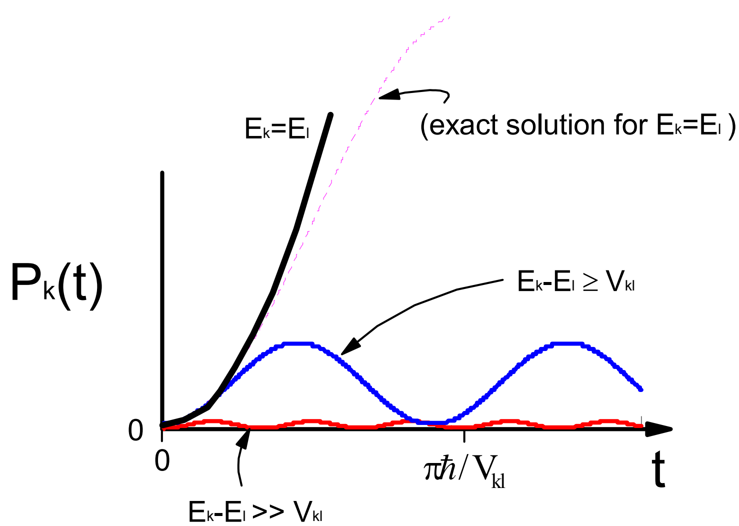
Clearly the P.T. result works for $V \ll \Delta$. (…not for degenerate systems)

The probability of transfer from $|\ell\rangle$ to $|k\rangle$ as a function of the energy level splitting $(E_k - E_\ell)$:



Area scales linearly with time.

Time-dependence:



Time dependence on resonance (Δ=0):

expand $\sin x = x - \frac{x^3}{3!} + \ \ldots$

$$P_k = \frac{V^2}{\Delta^2}\left(\frac{\Delta t}{\hbar} - \frac{\Delta^3 t^3}{6\hbar^3} + \ldots\right)^2$$
$$= \frac{V^2}{\hbar^2} t^2$$

This is unrealistic, but the expression shouldn't hold for Δ=0.

Long time limit: The sinc^2(x) function narrows rapidly with time giving a delta function:

$$\lim_{t\to\infty} \frac{\sin^2(ax/2)}{ax^2} = \frac{\pi}{2}\delta(x)$$

$$\lim_{t\to\infty} P_k(t) = \frac{2\pi|V_{k\ell}|^2}{\hbar}\delta(E_k - E_\ell)(t - t_0)$$

A probability that is linear in time suggests a transfer *rate* that is independent of time! This suggests that the expression may be useful to long times:

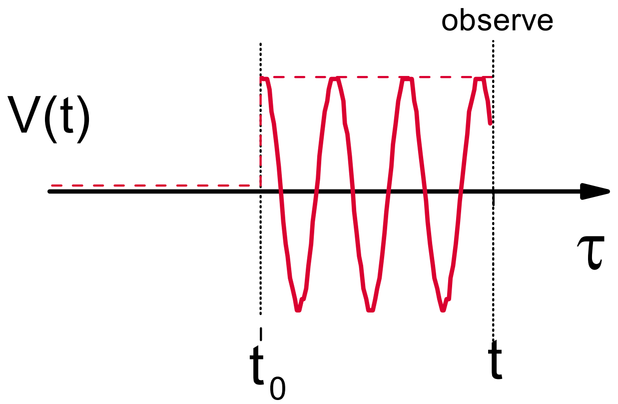
$$w_k(t) = \frac{\partial P_k(t)}{\partial t} = \frac{2\pi|V_{k\ell}|^2}{\hbar}\delta(E_k - E_\ell)$$

This is one statement of Fermi's Golden Rule, which describes relaxation rates from first order perturbation theory. We will show that this will give long time exponential relaxation rates.

(2) **Harmonic Perturbation**

Interaction of a system with an oscillating perturbation turned on at time $t_0 = 0$. This describes how a light field (monochromatic) induces transitions in a system through dipole interactions.

$$V(t) = V\cos\omega t = -\mu E_0 \cos\omega t$$



$$V_{k\ell}(t) = V_{k\ell}\cos\omega t$$
$$= \frac{V_{k\ell}}{2}\left[e^{i\omega t} + e^{-i\omega t}\right]$$

To first order, we have:

$$b_k = \langle k|\psi_I(t)\rangle = \frac{-i}{\hbar}\int_{t_0}^{t} d\tau\, V_{k\ell}(\tau)\, e^{i\omega_{k\ell}\tau}$$

$$= \frac{-iV_{k\ell}}{2\hbar}\int_{t_0}^{t} d\tau \left[e^{i(\omega_{k\ell}+\omega)\tau} - e^{i(\omega_{k\ell}-\omega)\tau}\right]$$

$$= \frac{-V_{k\ell}}{2\hbar}\left[\frac{e^{i(\omega_{k\ell}+\omega)t} - e^{i(\omega_{k\ell}+\omega)t_0}}{\omega_{k\ell}+\omega} + \frac{e^{i(\omega_{k\ell}-\omega)t} - e^{i(\omega_{k\ell}-\omega)t_0}}{\omega_{k\ell}-\omega}\right]$$

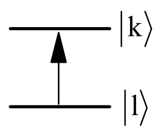
Setting $t_0 \to 0$ and using $e^{i\theta} - 1 = 2ie^{i\theta/2}\sin\theta/2$

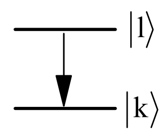
$$b_k = \frac{-iV_{k\ell}}{\hbar}\left[\frac{e^{i(\omega_{k\ell}-\omega)t/2}\sin\left[(\omega_{k\ell}-\omega)t/2\right]}{\omega_{k\ell}-\omega} + \frac{e^{i(\omega_{k\ell}+\omega)t/2}\sin\left[(\omega_{k\ell}+\omega)t/2\right]}{\omega_{k\ell}+\omega}\right]$$

Notice that these terms are only significant when

$\omega \approx \omega_{k\ell}$: *resonance*!

First Term	Second Term
max at: $\omega = +\omega_{k\ell}$	$\omega = -\omega_{k\ell}$
$E_k > E_\ell$	$E_k < E_\ell$
$E_k = E_\ell + \hbar\omega$	$E_k = E_\ell - \hbar\omega$
Absorption (resonant term)	Stimulated Emission (anti-resonant term)



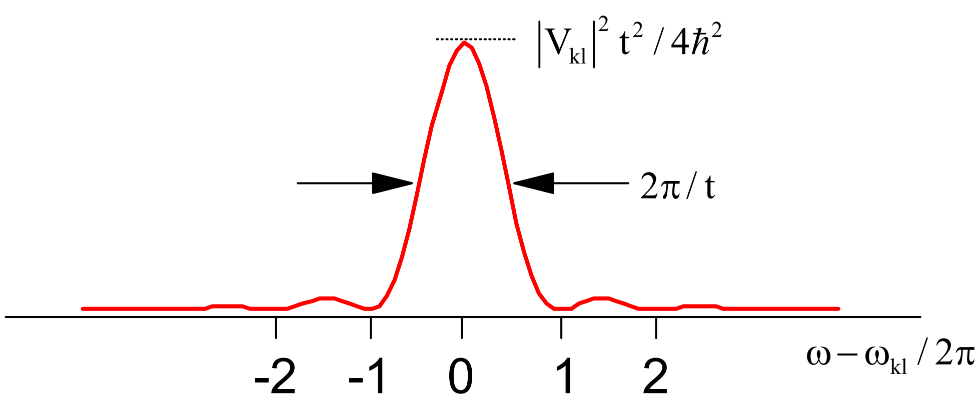


For the case where only absorption contributes, $E_k > E_\ell$, we have:

$$P_{k\ell} = |b_k|^2 = \frac{|V_{k\ell}|^2}{\hbar^2(\omega_{k\ell}-\omega)^2} \quad \sin^2\left[\tfrac{1}{2}(\omega_{k\ell}-\omega)t\right]$$

or $$\frac{E_0^2|\mu_{k\ell}|^2}{\hbar(\omega_{k\ell}-\omega)^2}\sin^2\left[\tfrac{1}{2}(\omega_{k\ell}-\omega)t\right]$$

The maximum probability for transfer is on resonance $\omega_{k\ell} = \omega$



We can compare this with the exact expression:

$$P_{k\ell} = |b_k|^2 = \frac{|V_{k\ell}|^2}{\hbar^2 (\omega_{k\ell} - \omega)^2 + |V_{k\ell}|^2} \quad \sin^2\left[\tfrac{1}{2\hbar}\sqrt{|V_{k\ell}|^2 + (\omega_{k\ell} - \omega)^2}\, t\right]$$

which points out that this is valid for couplings $|V_{k\ell}|$ that are small relative to the detuning $\Delta\omega = (\omega_{k\ell} - \omega)$.

Limitations of this formula:

By expanding $\sin x = x - \frac{x^3}{3!} + \ldots$, we see that on resonance $\Delta\omega = \omega_{k\ell} - \omega \to 0$

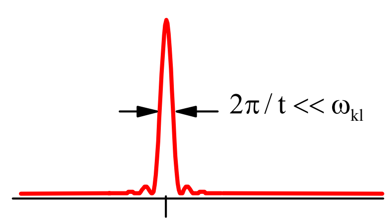
$$\lim_{\Delta\omega \to 0} P_k(t) = \frac{|V_{k\ell}|^2}{4\hbar^2} t^2$$

This clearly will not describe long-time behavior, but the expression is not valid for $\Delta\omega$=0. Nontheless, it will hold for small P_k, so

$$t << \frac{2\hbar}{V_{k\ell}} \qquad \text{(depletion of } |l\rangle \text{ neglected in first order P.T.)}$$

At the same time, we can't observe the system on too short a time scale. We need the field to make several oscillations for it to be a harmonic perturbation.

$$t > \frac{1}{\omega} \approx \frac{1}{\omega_{k\ell}}$$



These relationships imply that

$$V_{k\ell} << \hbar\omega_{k\ell}$$