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.

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 $V(t)$.

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

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

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

using

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

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

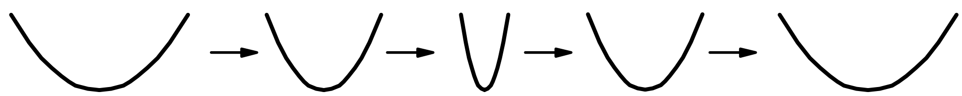
$$+\sum_m \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^{t} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1\, e^{-i\omega_{mk}\tau_2}\, V_{km}(\tau_2) e^{-i\omega_{\ell m}\tau_1}\, V_{m\ell}(\tau_1) \quad + \ldots \qquad \text{"second order"}$$

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

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

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.



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

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

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

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

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 $n \neq 0$:

$$b_n(t) = \frac{-i}{\hbar}\int_{t_0}^{t} d\tau \; V_{no}(\tau)\, e^{i\omega_{no}\tau}$$

$$= \frac{-i}{\hbar} A'\langle n|x^2|0\rangle \int_{-\omega}^{t\infty} d\tau\, e^{i\omega_{no}\tau} e^{-\tau^2/2\sigma^2}$$

$$E_n = \hbar\Omega_0\left(n + \tfrac{1}{2}\right); \quad \omega_{no} = n\Omega_0$$

$$b_n(t) = \frac{-i}{\hbar} A'\langle n|x^2|0\rangle \int_{-\infty}^{t\infty} d\tau\, e^{ni\Omega_0\tau - \tau^2/2\sigma^2}$$

$$\int_{-\infty}^{+\infty} e^{ax^2+bx+c}\,dx = \sqrt{\frac{-\pi}{a}}\, e^{c-\frac{1}{4}\frac{b^2}{a}}$$

$$= \frac{-i}{\hbar} A\langle n|x^2|0\rangle\, e^{-2n^2\sigma^2\Omega_0^2/4}$$

What about matrix element?

$$x^2 = \frac{\hbar}{m\omega_0}\left(a+a^\dagger\right)^2 = \frac{\hbar}{m\omega_0}\left(aa + a^\dagger a + aa^\dagger + a^\dagger a^\dagger\right)$$

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

$$\langle 2|x^2|0\rangle = \sqrt{2}\,\frac{\hbar}{m\Omega_0}$$

So,

$$b_2 = \frac{-\sqrt{2}i}{m\Omega_0} A\, e^{-2\sigma^2\Omega_0^2}$$

$$P_2 = |b_2|^2 = \frac{2\,A^2}{m^2\Omega_0^2} e^{-4\sigma^2\Omega_0^2}$$

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

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

for $P_2 \approx 0 \quad A^2 << m^2\Omega_0^2$

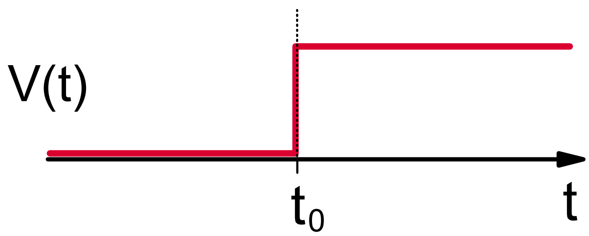
$A^2 << k_0$

First-Order Perturbation Theory

A number of important relationships in quantum mechanics that describe rate processes come from 1[st] 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

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

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

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

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

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

or writing this as we did in lecture 1:

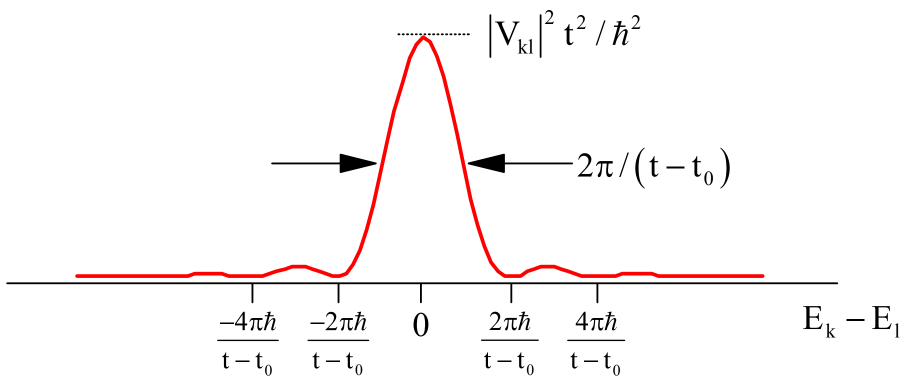
$$P_k = \frac{V^2}{\Delta^2}\sin^2(\Delta t/\hbar) \qquad \text{where } \Delta = \frac{E_k - E_l}{2}$$

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 small V.

The highest probability of transfer from $|\ell\rangle$ to $|k\rangle$ will be when their energies are the same $(E_k - E_\ell = 0)$.

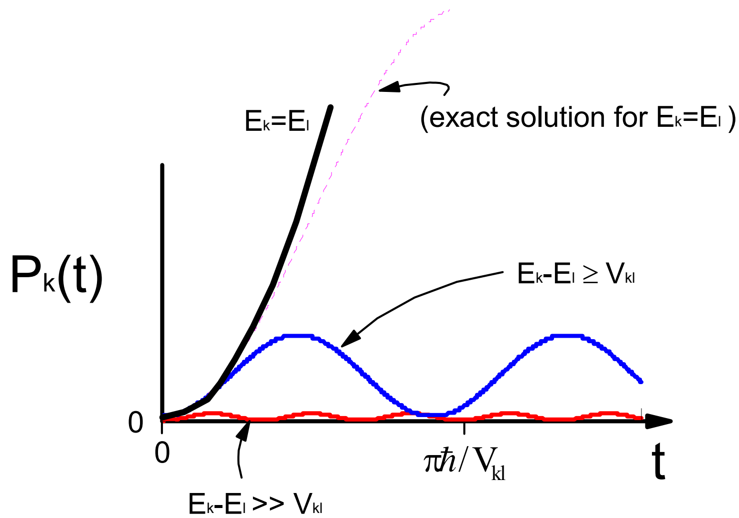


Area scales linearly with time.

Long time limit: The $\text{sinc}^2(x)$ function narrows rapidly with time giving a delta function:

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

Time-dependence:



Time dependence on resonance (Δ=0): expand $\sin x = x - \frac{x^3}{3!} + \ \ldots$

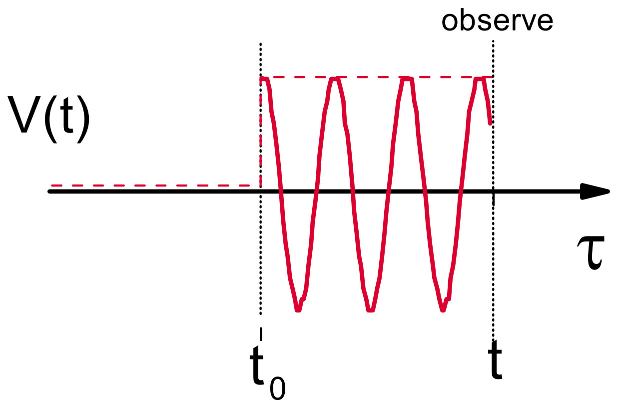
$$P_k = \frac{V^2}{\Delta^2}\left(\frac{\Delta t}{\hbar} - \frac{\Delta^3 t^3}{6\hbar^3} + \ldots \right)^2$$

$$= \frac{V^2}{\hbar^2} t^2$$

(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:

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

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

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

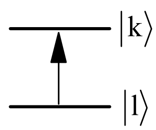
Setting $t_0 \to 0$ and using $e^{i\theta} - 1 = 2ie^{i\theta/2}\sin\theta/2$

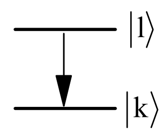
$$b_k = \frac{-iV_{k\ell}}{\hbar}\left[\frac{e^{i(\omega_{k\ell}-\omega)t/2}\sin\left[(\omega_{k\ell}-\omega)t/2\right]}{\omega_{k\ell}-\omega} + \frac{e^{i(\omega_{k\ell}+\omega)t/2}\sin\left[(\omega_{k\ell}+\omega)t/2\right]}{\omega_{k\ell}+\omega}\right]$$

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	Stimulated Emission
(resonant term)	(anti-resonant term)



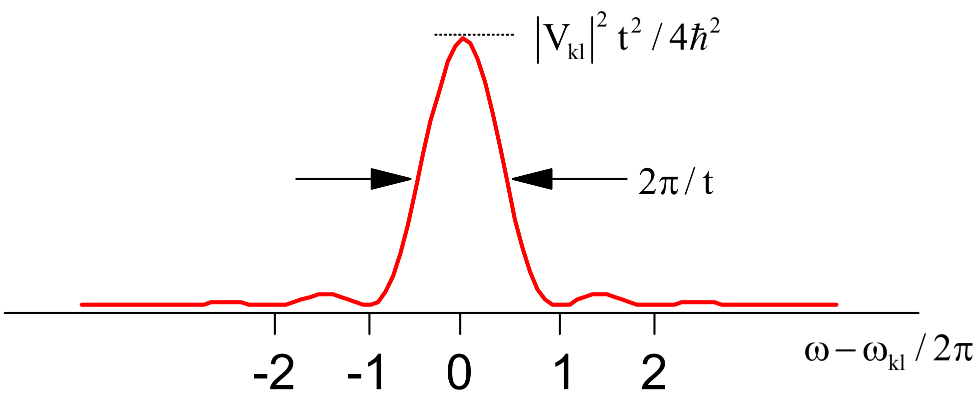


For the case where only absorption contributes, $E_k > E_\ell$, we have:

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

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

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



Limitations of this formula:

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

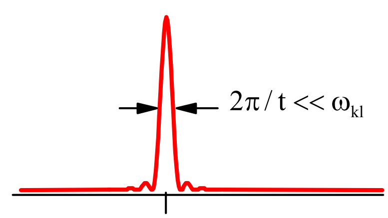
$$\lim_{\Delta \to 0} P_k(t) = \frac{|V_{k\ell}|^2}{4\hbar^2} t^2$$

This clearly will not describe long-time behavior: P_k is not > 1. It will hold for small P_k, so

$$t << \frac{2\hbar}{V_{k\ell}} \qquad \text{(depletion of } |1\rangle \text{ neglected in first order P.T.)}$$

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

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