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 can calculate the evolution of the wavefunction that results from \( V(t) : \)

\[
|\psi_f(t)\rangle = \sum_n b_n(t) |n\rangle
\]

using the coupled differential equations for the amplitudes of \( |n\rangle \). For a complex time-dependence or a system with many states to be considered, solving these equations isn’t practical.

Alternatively, we can choose to work directly with \( U_I(t,t_0) \), 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 \( V(t) : \)

\[
P_k(t) = |b_k(t)|^2 \quad \quad b_k(t) = \langle k | U_I(t,t_0) | \ell \rangle
\]

\[
b_k(t) = \langle k | \exp \left[ -\frac{i}{\hbar} \int_{t_0}^t d\tau V_I(\tau) \right] | \ell \rangle
\]
\[
    b_k(t) = \langle k | \ell \rangle - \frac{i}{\hbar} \int_{t_0}^{t_1} d\tau \langle k | V_1(\tau) | \ell \rangle + \left( \frac{-i}{\hbar} \right)^2 \int_{t_0}^{t_2} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \langle k | V_1(\tau_2) V_1(\tau_1) | \ell \rangle + \ldots
\]

using
\[
    \langle k | V_1(t) | \ell \rangle = \langle k | U^* V(t) U_0 | \ell \rangle = e^{-i\omega A t} V_{k\ell}(t)
\]

\[
    b_k(t) = \delta_{k\ell} - \frac{i}{\hbar} \int_{t_0}^{t_1} d\tau_1 e^{-i\omega A t_1} V_{k\ell}(\tau_1)
\]

“first order”

\[
    + \sum_m \left( \frac{-i}{\hbar} \right)^2 \int_{t_0}^{t_2} d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 e^{-i\omega A t_2} V_{km}(\tau_2) e^{-i\omega A t_1} V_{m\ell}(\tau_1) + \ldots
\]

“second order”

If \(|\psi_0\rangle\) is not an eigenstate, we only need to express it as a superposition of eigenstates,
\[
    |\psi_0\rangle = \sum_n b_n(0)|n\rangle \quad \text{and} \quad b_k(t) = \sum_n b_n(0) \langle k | U_j | n \rangle.
\]

Now there may be interference effects between the pathways initiating from different states:
\[
    P_k(t) = |c_k(t)|^2 = |b_k(t)|^2 = \left| \sum_n \langle k | b_n(t)|n \rangle \right|^2
\]

For perturbation theory, the time ordered integral is truncated at the appropriate order. Including only the first integral is first-order perturbation theory. Note that the first order term is just the solution to the differential equation that you get for direct coupling between \(|\ell\rangle\) and \(|k\rangle\):
\[
    \frac{\partial}{\partial t} b_k = -\frac{i}{\hbar} e^{-i\omega A t} V_{k\ell}(t) b_j(0)
\]
Also 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 $\omega_A$.

$$b_k(t) = -\frac{i}{\hbar} \int_{-\infty}^{+\infty} d\tau \ e^{-i\omega_A \tau} V_{kk}(\tau)$$

If the Fourier transform is defined as

$$\tilde{V}(\omega) \equiv \tilde{\mathcal{F}}[V(t)] = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} V(t) exp(i\omega t),$$

then

$$P_{kk} = |\tilde{V}(\omega_{kl})|^2.$$
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.

\[ H = T + V = \frac{p^2}{2m} + \frac{1}{2} k(t)x^2 \]

\[ V(t) \]

\[ k(t) = k_0 + \delta k(t) \quad k_0 = m\Omega^2 \quad \delta k(t) = \delta k_0 \exp \left( -\frac{(t-t_0)^2}{2\sigma^2} \right) \]

\[ H = H_0 + V(t) = \underbrace{\frac{p^2}{2m} + \frac{1}{2} k_0 x^2}_{H_0} + \underbrace{\frac{1}{2} \delta k_0 x^2 \exp \left( -\frac{(t-t_0)^2}{2\sigma^2} \right)}_{V(t)} \]

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

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 \( n \neq 0 \):

\[ b_n(t) = \frac{-i}{2\hbar} \int_{t_0}^{t} d\tau \ V_{n0}(\tau) \ e^{i\omega_n t} \]
\[ b_n(t) = \frac{-i}{2\hbar} \delta k_0 \langle n| x^2 |0 \rangle \int_{-\infty}^{\infty} d\tau \ e^{i\omega_{n0} \tau} e^{-\tau^2/2\sigma^2} \]

using \( \omega_{n0} = (E_n - E_0)/\hbar = n\Omega \)

\[ b_n(t) = \frac{-i}{2\hbar} \delta k_0 \langle n| x^2 |0 \rangle \int_{-\infty}^{\infty} d\tau \ e^{in\Omega \tau - \tau^2/2\sigma^2} \]

\[ b_n(t) = \frac{-i}{2\hbar} \delta k_0 \sqrt{2\pi\sigma} \langle n| x^2 |0 \rangle e^{-2n^2\sigma^2\Omega^2/4} \]

What about matrix element?

\[ x^2 = \frac{\hbar}{2m\Omega} (a + a^\dagger)^2 = \frac{\hbar}{2m\Omega} (aa + a^\dagger a + a^\dagger a^\dagger) \]

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,

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

So,

\[ b_2 = \frac{-i\sqrt{\pi} \delta k_0}{2m\Omega} e^{-2\sigma^2\Omega^2} \]
and \( P_2 = |b_2|^2 = \frac{\pi \delta k_0^2 \sigma^2}{2m^2 \Omega^2} e^{-4\sigma^2 \Omega^2} = \frac{\pi \sigma^2 \delta k_0^2}{2mk_0} e^{-4\sigma^2 \Omega^2} \)

From the exponential argument, significant transfer of amplitude occurs when the compression pulse is short compared to the vibrational period.

\[ \sigma \ll \frac{1}{\Omega} \]

**Validity:** First order doesn’t allow for feedback and \( b_n \) can’t change much from its initial value.

for \( P_2 \ll 1 \)

\[ \frac{\pi \sigma^2 \delta k_0^2}{2mk_0} \ll 1 \]

or \( \sigma^2 \Omega^2 \frac{\pi}{2} \left( \frac{\delta k_0^2}{k_0^2} \right) \ll 1 \)

Generally, the perturbation \( \delta k(t) \) must be small compared to \( k_0 \), but it should also work well for the impulsive shock limit (\( \sigma \Omega \ll 1 \)).
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:

**Constant Perturbation**  (Step-Function Perturbation)

\[ |\psi(-\infty)\rangle = |\ell\rangle . \]

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:

\[ \langle k | U_0^\dagger V U_0 | \ell \rangle = V e^{i\omega_k(t-t_0)} \]

\[ b_k = \delta_{k\ell} - \frac{i}{\hbar} \int_{t_0}^t d\tau \ e^{i\omega_k(\tau-t_0)} V_{k\ell} \]

\[ V_{k\ell} \text{ independent of time} \]

setting \( t_0 = 0 \) we have

\[ b_k = \delta_{k\ell} + \frac{-i}{\hbar} V_{k\ell} \int_0^t d\tau \ e^{i\omega_k\tau} \]

\[ = \delta_{k\ell} + \frac{-V_{k\ell}}{E_k - E_\ell} \left[ \exp(i\omega_k\tau) - 1 \right] \]

\[ = \delta_{k\ell} + \frac{-2iV_{k\ell}e^{i\omega_k\tau/2}}{E_k - E_\ell} \sin(\omega_k\tau/2) \]

\[ \text{using } e^{i\theta} - 1 = 2i e^{i\theta/2} \sin \frac{\theta}{2} \]

For \( k \neq \ell \) we have

\[ P_k = |b_k|^2 = \frac{4|V_{k\ell}|^2}{|E_k - E_\ell|^2} \sin^2 \frac{1}{2} \omega_k \tau \]
Writing this as we did in Lecture 1:

\[ P_k = \frac{V^2}{\Delta^2} \sin^2 \left( \frac{\Delta t}{\hbar} \right) \quad \text{where} \quad \Delta = \frac{E_k - E_l}{2} \]

Compare this with the exact result we have for the two-level problem:

\[ P_k = \frac{V^2}{V^2 + \Delta^2} \sin^2 \left( \sqrt{\Delta^2 + V^2} \frac{t}{\hbar} \right) \]

Clearly the perturbation theory result works for \( V \ll \Delta \).

We can also write the first-order result as

\[ P_k = \frac{V^2 t^2}{\hbar^2} \sin^2 \left( \frac{\Delta t}{2\hbar} \right) \quad \text{where} \quad \text{sin c}(x) = \frac{\sin(x)}{x} \]

\[ \lim_{x \to 0} \text{sin c}(x) = 1 \quad \text{so} \quad \lim_{\Delta \to 0} P_k = \frac{V^2 t^2}{\hbar^2} \]

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

Area scales linearly with time.

Time-dependence:
Time dependence on resonance ($\Delta=0$):

\[
\sin x = x - \frac{x^3}{3!} + \ldots
\]

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

\[
= \frac{V^2}{\hbar^2} t^2
\]

This is unrealistic, but the expression shouldn’t hold for $\Delta=0$.

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

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

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

The delta function enforces energy conservation, saying that the energies of the initial and target state must be the same in the long time limit.

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—the state-to-state form—which describes relaxation rates from first order perturbation theory. We will show that this rate properly describes long time exponential relaxation rates that you would expect from the solution to $dP/dt = -wP$. 
**Slowly Applied (Adiabatic) Perturbation**

Our perturbation was applied suddenly at $t > t_0$ (step function)

$$V(t) = \theta(t - t_0)V(t)$$

This leads to unphysical consequences—you generally can’t turn on a perturbation fast enough to appear instantaneous. Since first-order P.T. says that the transition amplitude is related to the Fourier Transform of the perturbation, this leads to additional Fourier components in the spectral dependence of the perturbation—even for a monochromatic perturbation!

So, let’s apply a perturbation slowly . . .

$$V(t) = V e^{\eta t}$$

Here $\eta$ is a small positive number.

The system is prepared in state $|\ell\rangle$ at $t = -\infty$. Find $P_k(t)$.

$$b_k = \langle k | U_j | \ell \rangle = \frac{-i}{\hbar} \int_{-\infty}^{t} d\tau e^{i\omega_k \tau} \langle k | V | \ell \rangle e^{\eta \tau}$$

$$b_k = \frac{-iV_{k\ell}}{\hbar} \frac{\exp[\eta t + i\omega_k t]}{\eta + i\omega_k}$$

$$= V_{k\ell} \frac{\exp[\eta t + i(E_k - E_\ell) / \hbar]}{E_k - E_\ell + i\eta \hbar}$$

$$P_k = |b_k|^2 = \frac{|V_{k\ell}|^2 \exp[2\eta t]}{\eta^2 + \omega_k^2} = \frac{|V_{k\ell}|^2 \exp[2\eta t]}{(E_k - E_\ell)^2 + (\eta \hbar)^2}$$

This is a Lorentzian lineshape in $\omega_{k\ell}$ with width $2\eta \hbar$. 
The gradually turned on perturbation has a width dependent on the turn-on rate, and is independent of time. (The amplitude grows exponentially in time.) Notice, there are no nodes in $P_k$.

$\eta^{-1}$ is the effective turn-on time of the perturbation:

Now, let’s calculate the transition rate:

$$w_{kl} = \frac{\partial P_k}{\partial t} = \frac{|V_{k\ell}|^2}{\hbar^2} \frac{2\eta \omega_a^2}{\eta^2 + \omega_a^2}$$

Look at the adiabatic limit; $\eta \to 0$.

setting $e^{2\eta t} \to 1$; and using

$$\lim_{\eta \to 0} \frac{\eta}{\eta^2 + \omega_a^2} = \frac{\pi}{2} \delta(\omega_a)$$

$$w_{k\ell} = \frac{2\pi}{\hbar^2} |V_{k\ell}|^2 \delta(\omega_a) = \frac{2\pi}{\hbar} |V_{k\ell}|^2 \delta(E_k - E_{\ell})$$

We get Fermi’s Golden Rule—indepedent of how perturbation is introduced!
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.

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

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

To first order, we have:

$$b_k = \langle k | \psi_i (t) \rangle = \frac{-i}{\hbar} \int_{t_0}^t d\tau V_{kl}(\tau) e^{i \omega_k \tau}$$

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

setting $t_0 \to 0$

$$= \frac{-V_{kl}}{2\hbar} \left[ \frac{e^{i(\omega_k + \omega)t} - 1}{\omega_k + \omega} + \frac{e^{i(\omega_k - \omega)t} - 1}{\omega_k - \omega} \right]$$

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

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

Notice that these terms are only significant when

$$\omega \approx \omega_{kl}: \text{ resonance!}$$
First Term
\[
\text{max at: } \omega = +\omega_{k\ell} \\
E_k > E_{\ell} \\
E_k = E_{\ell} + \hbar \omega \\
\text{Absorption (resonant term)} \\
\]  

Second Term
\[
\omega = -\omega_{k\ell} \\
E_k < E_{\ell} \\
E_k = E_{\ell} - \hbar \omega \\
\text{Stimulated Emission (anti-resonant term)} \\
\]

For the case where only absorption contributes, \(E_k > E_{\ell}\), we have:
\[
P_{kl} = |b_k|^2 = \frac{|V_{kl}|^2}{\hbar^2 \left(\omega_{k\ell} - \omega\right)^2} \sin^2 \left[\frac{1}{2} \left(\omega_{k\ell} - \omega\right) t\right]
\]

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

We can compare this with the exact expression:
\[
P_{kl} = |b_k|^2 = \frac{|V_{kl}|^2}{\hbar^2 \left(\omega_{k\ell} - \omega\right)^2 + |V_{kl}|^2} \sin^2 \left[\frac{1}{2\hbar} \sqrt{|V_{kl}|^2 + (\omega_{k\ell} - \omega)^2} \ t\right]
\]

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

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 $\Delta \omega = \omega_{kl} - \omega \to 0$

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

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

$$t << \frac{2\hbar}{V_{kl}}$$

(depletion of $|\ell\rangle$ 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.

$$t > \frac{1}{\omega} \approx \frac{1}{\omega_{kl}}$$

These relationships imply that

$$V_{kl} << \hbar \omega_{kl}$$

Adiabatic Harmonic Perturbation:

What happens if we slowly turn on the harmonic interaction?

$$V(t) = V e^{i\eta} \cos \omega t$$

$$b_k = \frac{-i}{\hbar} \int_{-\infty}^{t} d\tau V_{kl} e^{i\omega_{kl} \tau + \eta \tau} \left[ \frac{e^{i\eta} + e^{-i\eta}}{2} \right]$$

$$= V_{kl} e^{i\eta} \left[ \frac{e^{i(\omega_{kl}+\omega)\tau}}{-(\omega_{kl}+\omega) + i\eta} + \frac{e^{i(\omega_{kl}-\omega)\tau}}{-(\omega_{kl} - \omega) + i\eta} \right]$$
Again, we have a resonant and anti-resonant term, which are now broadened by $\eta$.

If we only consider absorption:

$$P_k = |b_k|^2 = \frac{|V_{kl}|^2}{4\hbar^2} e^{2\eta t} \frac{1}{(\omega_{kl} - \omega)^2 + \eta^2}$$

which is the Lorentzian lineshape centered at $\omega_{kl} = \omega$ with width $\Delta \omega = 2\eta$.

Again, we can calculate the adiabatic limit, setting $\eta \to 0$. We will calculate the rate of transitions $\omega_{kl} = \partial P_k / \partial t$. But let’s restrict ourselves to long enough times that the harmonic perturbation has cycled a few times (this allows us to neglect cross terms) → resonances sharpen.

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