

2.4 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 \( V(t) \):

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

(2.111)

- 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:

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

(2.112)

where

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

(2.113)

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 \( (|b_k(t)| \approx |b_k(0)|; |V| \ll |E_k - E_n|) \) As we’ll see, the results we obtain from perturbation theory are widely used for spectroscopy, condensed phase dynamics, and relaxation.

**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 \( V(t) \).

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

(2.114)
\[ b_k(t) = \left\langle k \left| \exp \left[ -i \int_0^t d\tau V_i(\tau) \right] \right| \ell \right\rangle \]  

(2.115)

\[ b_k(t) = \langle k | \ell \rangle - \frac{i}{\hbar} \int_0^t d\tau \langle k | V_i(\tau) | \ell \rangle \]

\[ + \left( \frac{-i}{\hbar} \right)^2 \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \langle k | V_i(\tau_2) V_i(\tau_1) | \ell \rangle + \ldots \]  

using

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

(2.117)

So,

\[ b_k(t) = \delta_{k\ell} - \frac{i}{\hbar} \int_0^t d\tau_1 e^{-i\omega_k \tau_1} V_{k\ell}(\tau_1) \]

"first order"  

(2.118)

\[ + \sum_m \left( \frac{-i}{\hbar} \right)^2 \int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 e^{-i\omega_{km} \tau_2} \left( V_{km}(\tau_2) e^{-i\omega_{m\ell} \tau_1} V_{m\ell}(\tau_1) \right) + \ldots \]  

"second order"  

(2.119)

The first-order term allows only direct transitions between \(|\ell\rangle\) and \(|k\rangle\), as allowed by the matrix element in \(V\), whereas the second-order term accounts for transitions occurring through all possible intermediate states \(|m\rangle\). For perturbation theory, the time ordered integral is truncated at the appropriate order. Including only the first integral is first-order perturbation theory. The order of perturbation theory that one would extend a calculation should be evaluated initially by which allowed pathways between \(|\ell\rangle\) and \(|k\rangle\) you need to account for and which ones are allowed by the matrix elements.

For first order perturbation theory, the expression in eq. (2.118) is the solution to the differential equation that you get for direct coupling between \(|\ell\rangle\) and \(|k\rangle\):

\[ \frac{\partial}{\partial t} b_k = -\frac{i}{\hbar} e^{-i\omega_k t} V_{k\ell}(t) b_\ell(0) \]  

(2.120)
This indicates that the solution doesn’t allow for the feedback between $|\ell\rangle$ and $|k\rangle$ that accounts for changing populations. This is the reason we say that validity dictates $|b_k(t)| \approx |b_k(0)|$.

If $|\psi_0\rangle$ is not an eigenstate, we only need to express it as a superposition of eigenstates,

$$|\psi_0\rangle = \sum_n b_n(0) |n\rangle$$

and

$$b_k(t) = \sum_n b_n(0) \langle k | U_j | n \rangle.$$  \hspace{1cm} (2.121)

Now there may be interference effects between the pathways initiating from different states:

\[ P_k(t) = |c_k(t)|^2 = |b_k(t)|^2 = \left| \sum_n \langle k | b_n(t) | n \rangle \right|^2 \] \hspace{1cm} (2.122)

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 $\omega_{\ell k}$.

\[ b_k(t) = -\frac{i}{\hbar} \int_{-\infty}^{+\infty} d\tau \ e^{-i\omega_{\ell k} \tau} V_{k \ell}(\tau) \] \hspace{1cm} (2.123)

If the Fourier transform is defined as

\[ \tilde{V}(\omega) \equiv \tilde{F}[V(t)] = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} dt \ V(t) \exp(i\omega t), \] \hspace{1cm} (2.124)

then

\[ \tilde{V}_{k \ell}(\omega) \] \hspace{1cm} (2.125)
**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 its force constant.

![Diagram](https://via.placeholder.com/150)

First write the Hamiltonian:

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

(2.126)

Now partition it according to \( H = H_0 + V(t) \):

\[
k(t) = k_0 + \delta k(t)
\]

\[
k_0 = m\Omega^2
\]

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

(2.127)

\[
H= \underbrace{\frac{p^2}{2m} + \frac{1}{2} k_0x^2 + \frac{1}{2} \delta k_0 x^2 \exp\left(-\frac{(t-t_0)^2}{2\sigma^2}\right)}_{H_0} + \underbrace{V(t)}_{V(t)}
\]

(2.128)

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

(2.129)
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 $n \neq 0$:

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

(2.130)

Using $\omega_{n0} = (E_n - E_0)/\hbar = n\Omega$:

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

(2.131)

So,

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

(2.132)

Here we used:

What about the matrix element?

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

(2.133)

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,

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

(2.134)

So,

$$b_2 = -i \sqrt{\pi} \delta k_0 \sigma \ e^{-2\sigma^2\Omega^2}$$

(2.135)
and

\[ P_2 = \left| b_2 \right|^2 = \frac{\pi \delta k_0^2 \sigma^2}{2m^2 \Omega^2} e^{-4\sigma^2 \Omega^2} = \frac{\sigma^2 \Omega^2}{2} \left( \frac{\delta k_0^2}{k_0^2} \right) e^{-4\sigma^2 \Omega^2} \]  \hspace{1cm} (2.136)

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

\[ \sigma \ll \frac{1}{\Omega} \]  \hspace{1cm} (2.137)

**Validity:** First order perturbation theory doesn’t allow for \( b_n \) to change much from its initial value. For \( P_2 \ll 1 \)

\[ \sigma^2 \Omega^2 \frac{\pi}{2} \left( \frac{\delta k_0^2}{k_0^2} \right) \ll 1 \]  \hspace{1cm} (2.138)

Generally, the perturbation \( \delta k(t) \) must be small compared to \( k_0 \), i.e. \( |H_0| >> |\nu| \), 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 1\textsuperscript{st} order perturbation theory. 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:

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

\[
b_k = \delta_{k\ell} - \frac{i}{\hbar} \int_{t_0}^t d\tau e^{i\omega_k (\tau-t_0)}V_{k\ell}(\tau)
\] (2.1)

Here \( V_{k\ell} \) is independent of time. Now, assuming \( k \neq \ell \) and setting \( t_0 = 0 \) we have

\[
b_k = -\frac{i}{\hbar} V_{k\ell} \int_0^t d\tau e^{i\omega_k \tau}
\] (2.140)

\[
= -\frac{V_{k\ell}}{E_k - E_\ell} \left[ \exp(i\omega_k t) - 1 \right]
\] (2.141)

\[
= -\frac{2iV_{k\ell} e^{i\omega_k t/2}}{E_k - E_\ell} \sin\left(\omega_k t / 2\right)
\] (2.142)

Where I used \( e^{i\theta} - 1 = 2i e^{i\theta/2} \sin(\theta/2) \). Now
\[ P_k = |b_k|^2 = \frac{4|V_{ki}|^2}{|E_k - E_i|^2} \sin^2 \frac{1}{2} \omega_{ki} t \]  

(2.143)

Writing this as we did in Lecture 1:

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

(2.144)

where \( \Delta = (E_k - E_i)/2 \). Compare this with the exact result we have for the two-level problem:

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

(2.145)

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

We can also write the first-order result as

\[ P_k = \frac{V^2 t^2}{\hbar^2} \text{sinc}^2 \left( \Delta t / 2\hbar \right) \]  

(2.146)

where \( \text{sinc}(x) = \sin(x)/x \). Since \( \lim_{x \to 0} \text{sinc}(x) = 1 \),

\[ \lim_{\Delta \to 0} P_k = \frac{V^2 t^2}{\hbar^2} \]  

(2.147)

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

Since the energy spread of states to which transfer is efficient scales approximately as \( E_k - E_i < 2\pi\hbar/t \), this observation is sometimes referred to as an uncertainty relation.
with $\Delta E \cdot \Delta t \geq 2\pi \hbar$. However, remember that this is really just an observation of the principles of Fourier transforms, that frequency can only be determined by the length of the time period over which you observe oscillations. Since time is not an operator, it is not a true uncertainly relation like $\Delta p \cdot \Delta x \geq 2\pi \hbar$.

Now turning to the time-dependence:

The quadratic growth for $\Delta=0$ is certainly unrealistic (at least for long times), but the expression shouldn’t hold for what is a “strong coupling” case $\Delta=0$. However, let’s continue looking at this behavior. In the long time limit, the $\text{sinc}^2(x)$ function narrows rapidly with time giving a delta function:

$$\lim_{t \to \infty} \frac{\sin^2(ax/2)}{ax^2} = \frac{\pi}{2} \delta(x)$$  \hspace{1cm} (2.148)

$$\lim_{t \to \infty} P_k(t) = \frac{2\pi |V_{kl}|^2}{\hbar} \delta(E_k - E_l) t$$  \hspace{1cm} (2.149)

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.

What is interesting in eq. (2.149) is that we see a probability growing linearly in time. This suggests a transfer rate that is independent of time, as expected for simple first order kinetics:
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 \( \frac{dP}{dt} = -wP \).
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. \( \eta^{-1} \) is the effective turn-on time of the perturbation.

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

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

\[
b_k = \frac{-i V_{k\ell}}{\hbar} \frac{\exp[\eta t + i \omega_{k\ell} t]}{\eta + i \omega_{k\ell}}
\]

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

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

This is a Lorentzian lineshape in \( \omega_{k\ell} \) with width \( 2\eta \hbar \).
Gradually Applied Perturbation

Step Response Perturbation

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 $P_k$.

Now, let’s calculate the transition rate:

$$w_{kl} = \frac{\partial P_k}{\partial t} = \frac{\left| V_{kl} \right|^2}{\hbar^2} \frac{2\eta e^{2\eta t}}{\eta^2 + \omega_{kl}^2}$$

Look at the adiabatic limit: $\eta \to 0$. Setting $e^{2\eta t} \to 1$ and using

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

$$w_{kl} = \frac{2\pi}{\hbar^2} \left| V_{kl} \right|^2 \delta(\omega_{kl}) = \frac{2\pi}{\hbar} \left| V_{kl} \right|^2 \delta(E_k - E_l)$$

We get Fermi’s Golden Rule—indepenent 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. Again, we are looking to calculate the transition probability between states $\ell$ and $k$:

$$V(t) = V \cos \omega t = -\mu E_0 \cos \omega t$$  \hspace{1cm} (2.151)

$$V_{\ell\ell} (t) = V_{\ell\ell} \cos \omega t$$

$$= \frac{V_{\ell\ell}}{2} \left[ e^{i\omega t} + e^{-i\omega t} \right]$$  \hspace{1cm} (2.152)

To first order, we have:

$$b_k = \langle k \mid \psi(t) \rangle = \frac{-i}{\hbar} \int_0^t d\tau V_{\ell\ell}(\tau) e^{i\omega_k \tau}$$

$$= \frac{-iV_{\ell\ell}}{2\hbar} \int_0^t d\tau \left[ e^{i(\omega_k + \omega)\tau} - e^{i(\omega_k - \omega)\tau} \right]$$

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

setting $t_0 \rightarrow 0$ (2.153)

Now, using $e^{\theta} - 1 = 2i e^{i\theta/2} \sin(\theta/2)$ as before:

$$b_k = \frac{-iV_{\ell\ell}}{\hbar} \left[ \frac{e^{i(\omega_k - \omega)t/2} \sin[(\omega_k - \omega) t / 2]}{\omega_k - \omega} + \frac{e^{i(\omega_k + \omega)t/2} \sin[(\omega_k + \omega) t / 2]}{\omega_k + \omega} \right]$$  \hspace{1cm} (2.154)

Notice that these terms are only significant when $\omega \approx \omega_{\ell\ell}$. As we learned before, resonance is required to gain significant transfer of amplitude.
For the case where only absorption contributes, $E_k > E_\ell$, we have:

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

or

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

We can compare this with the exact expression:

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

which points out that this is valid for couplings $|V_{k\ell}|$ that are small relative to the detuning $\Delta \omega = (\omega_{k\ell} - \omega)$. 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 \( \Delta \omega = \omega_{kl} - \omega \to 0 \)

\[
\lim_{\Delta \omega \to 0} P_k(t) = \frac{\left| V_{kl} \right|^2}{4\hbar^2} t^2
\]  

(2.157)

This clearly will not describe long-time behavior. This is a result of 1st order perturbation theory not treating the depletion of \( \left| \ell \right> \). However, it will hold for small \( P_k \), so we require

\[
t << \frac{2\hbar}{V_{kl}}
\]  

(2.158)

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.

\[
t > \frac{1}{\omega} = \frac{1}{\omega_{kl}}
\]  

(2.159)

These relationships imply that

\[
V_{kl} << \hbar \omega_{kl}
\]  

(2.160)
**Adiabatic Harmonic Perturbation**

What happens if we slowly turn on the harmonic interaction?

\[ V(t) = V e^{\eta t} \cos \omega t \]

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

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

Again, we have a resonant and anti-resonant term, which are now broadened by \( \eta \). If we only consider absorption:

\[
P_k = \left| b_k \right|^2 = \frac{V_{k\ell}^2 e^{2\eta t} 1}{4\hbar^2} \frac{1}{(\omega_{k\ell} - \omega)^2 + \eta^2}
\]

which is the Lorentzian lineshape centered at \( \omega_{k\ell} = \omega \) with width \( \Delta\omega = 2\eta \). Again, we can calculate the adiabatic limit, setting \( \eta \to 0 \). We will calculate the rate of transitions \( \omega_{k\ell} = \partial P_k / \partial t \). 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) \( \to \) resonances sharpen.

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