TIME-DEPENDENT HAMILTONIAN

Mixing of eigenstates by a time-dependent interaction potential

For many time-dependent problems, most notably in spectroscopy, we often can partition the time-dependent Hamiltonian into a time-independent part that we can describe exactly and a time-dependent part

\[ H = H_0 + V(t) \]  

\( H_0 \): time-independent; \( V(t) \): time-dependent potential, often an external field. If the magnitude of \( V \) is considerably less than \( H_0 \), then there is a straightforward approach to describing the time-evolving wavefunction for the system in terms of the eigenstates and energy eigenvalues of \( H_0 \).

We know

\[ H_0 |n\rangle = E_n |n\rangle. \]  

The state of the system \((t = t_0)\) can be expressed as a superposition of these eigenstates:

\[ |\psi(t_0)\rangle = \sum_n c_n |n\rangle, \]  

as can the system for longer times,

\[ |\psi(t)\rangle = \sum_n c_n(t) |n\rangle \]  

The T.D.S.E. can be used to find an equation of motion for the expansion coefficients

\[ c_k(t) = \langle k | \psi(t) \rangle \]  

Starting with

\[ \frac{\partial |\psi\rangle}{\partial t} = -\frac{i}{\hbar} H |\psi\rangle \]  

\[ \frac{\partial c_k(t)}{\partial t} = -\frac{i}{\hbar} \langle k | H | \psi(t) \rangle \]  

inserting \( \sum_n |n\rangle \langle n| = 1 \)

\[ = -\frac{i}{\hbar} \sum_n \langle k | H | n \rangle c_n(t) \]
\[
\begin{align*}
\psi(n) & = -\frac{i}{\hbar} \sum_n \langle k | (H_0 + V(t)) | n \rangle c_n(t) \\
& = -\frac{i}{\hbar} \sum_n [E_n \delta_{kn} + V_{kn}(t)] c_n(t)
\end{align*}
\]

substituting eq. 1.

or,

\[
\frac{\partial c_k(t)}{\partial t} + \frac{i}{\hbar} E_k c_k(t) = -\frac{i}{\hbar} \sum_n V_{kn}(t) c_n(t)
\]

(9)

If we make a substitution \( c_m(t) = e^{-i\omega_m t/\hbar} b_m(t) \), which defines a slightly different expansion coefficient we can simplify considerably. Notice that \( |b_k(t)|^2 = |c_k(t)|^2 \). Also, \( b_k(0) = c_k(0) \). It is easy to calculate \( b_k(t) \) and then add in the extra oscillatory term at the end.

Now eq. 9 becomes

\[
e^{-iE_k t/\hbar} \frac{\partial b_k}{\partial t} = -\frac{i}{\hbar} \sum_n V_{kn}(t) e^{-iE_k t/\hbar} b_n(t)
\]

or

\[
i\hbar \frac{\partial b_k}{\partial t} = \sum_n V_{kn}(t) e^{-i\omega_k t} b_n(t)
\]

This equation is an exact solution. It is a set of coupled differential equations that describe how probability amplitude moves through eigenstates due to a time-dependent potential. Except in simple cases, these equations can’t be solved analytically, but it’s often straightforward to integrate numerically.
**Resonant Driving of Two-level System**

Let’s describe what happens when you drive a two-level system with an oscillating potential.

\[ V(t) = V \cos \omega t = Vf(t) \]

This is what you expect for an electromagnetic field interacting with charged particles: dipole transitions. The electric field is

\[ \overline{E}(t) = \overline{E}_0 \cos \omega t \]

For a particle with charge \( q \) in a field \( \overline{E} \), the force on the particle is

\[ \overline{F} = q \overline{E} \]

which is the gradient of the potential

\[ F_x = -\frac{\partial V}{\partial x} = qE_x \quad \Rightarrow \quad V = -qE_x x \]

\( qx \) is just the \( x \) component of the dipole moment \( \mu \). So matrix elements in \( V \) look like:

\[ \langle k | V(t) | \ell \rangle = -qE_x \langle k | x | \ell \rangle \cos \omega t \]

More generally,

\[ V = -\overline{E} \cdot \overline{\mu} . \]

So,

\[ V(t) = V \cos \omega t = -\overline{E}_0 \cdot \overline{\mu} \cos \omega t . \]

\[ V_{k\ell}(t) = V_{k\ell} \cos \omega t = -\overline{E}_0 \cdot \overline{\mu}_{k\ell} \cos \omega t \]

We will now couple our two states \(|k\rangle + |\ell\rangle \) with the oscillating field. Let’s ask if the system starts in \(|\ell\rangle \) what is the probability of finding it in \(|k\rangle \) at time \( t \)?
The system of differential equations that describe this situation are:

\[ i \hbar \frac{\partial}{\partial t} b_k(t) = \sum_n b_n(t) V_{kn}(t) e^{-i\omega_n t} = \sum_n b_n(t) V_{kn} e^{-i\omega_n t} \times \frac{i}{2} (e^{-i\omega t} + e^{+i\omega t}) \]

\[ i \hbar \dot{b}_k = \frac{1}{2} b_f V_{kf} \left[ e^{i(\omega_k - \omega)t} + e^{i(\omega_k + \omega)t} \right] + \frac{1}{2} b_k V_{kk} \left[ e^{i\omega_n t} + e^{-i\omega_n t} \right] = (1) \text{ and } (2) \]

\[ i \hbar \dot{b}_f = \frac{1}{2} b_f V_{ff} \left[ e^{i\omega t} + e^{-i\omega t} \right] + \frac{1}{2} b_k V_{fk} \left[ e^{i(\omega_k - \omega)t} + e^{i(\omega_k + \omega)t} \right] = (3) \text{ and } (4) \]

or

\[ \left[ e^{-i(\omega_k + \omega)t} + e^{-i(\omega_k - \omega)t} \right] \]

We can drop (2) and (3). For our case, \( V_{ii} = 0 \).

We also make the **secular approximation** (rotating wave approximation) in which the nonresonant terms are dropped. When \( \omega_{kf} \approx \omega \), terms like \( e^{i\omega t} \) or \( e^{i(\omega_k + \omega)t} \) oscillate very rapidly and so don’t contribute much to change of \( c_n \).

So we have:

\[ \dot{b}_k = \frac{1}{2\hbar} b_f V_{kf} e^{i(\omega_k - \omega)t} \]

(1)

\[ \dot{b}_f = \frac{1}{2\hbar} b_k V_{kf} e^{-i(\omega_k - \omega)t} \]

(2)

Note that the coefficients are oscillating out of phase with one another.

Now if we differentiate (1):

\[ \ddot{b}_k = \frac{1}{2\hbar} \left[ \dot{b}_f V_{kf} e^{i(\omega_k - \omega)t} + i(\omega_k - \omega) b_f V_{kf} e^{i(\omega_k - \omega)t} \right] \]

(3)

Rewrite (1):

\[ b_f = \frac{2i\hbar}{V_{kf}} \dot{b}_k e^{-i(\omega_k - \omega)t} \]

(4)

and substitute (4) and (2) into (3), we get linear second order equation for \( b_k \).
\[ \ddot{b}_k - i (\omega_{k\ell} - \omega) \dot{b}_k + \frac{|V_{k\ell}|^2}{4\hbar^2} b_k = 0 \]

This is just the second order differential equation for a damped harmonic oscillator:

\[ a\ddot{x} + b\dot{x} + cx = 0 \]

\[ x = e^{-(b/2a)t} \left( A \cos \mu t + B \sin \mu t \right) \quad \mu = \frac{1}{2\hbar} \left[ 4ac - b^2 \right]^{1/2} \]

With a little more work, and remembering the initial conditions \( b_k(0) = 0 \) and \( b_\ell(0) = 1 \), we find

\[ P_k = |b_k(t)|^2 = \frac{|V_{k\ell}|^2}{|V_{k\ell}|^2 + \hbar^2 (\omega_{k\ell} - \omega)^2} \sin^2 \Omega t \]

where \( \Omega_k = \frac{1}{2\hbar} \left[ |V_{k\ell}|^2 + \hbar^2 (\omega_{k\ell} - \omega)^2 \right]^{1/2} \)

\[ P_\ell = 1 - |b_k|^2 \]

The amplitude oscillates back and forth between the two states at a frequency dictated by the coupling between them.

Note a result we will return to later: Electric fields couple states, creating coherences!

**Resonance:** To get transfer of probability amplitude you need the driving field to be at the same frequency as the energy splitting.

On resonance, you always drive probability amplitude entirely from one state to another.
Efficiency of driving between $\ell$ and $k$ states drops off with detuning.