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5.74 Introductory Quantum Mechanics II
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2.1. TIME-DEPENDENT HAMILTONIAN

Mixing of eigenstates by a time-dependent 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

$$H = H_0 + V(t) \quad (2.1)$$

Here H_0 is time-independent and $V(t)$ is a time-dependent potential, often an external field. Nitzan, Sec. 2.3., offers a nice explanation of the circumstances that allow us to use this approach. It arises from partitioning the system into internal degrees of freedom in H_0 and external degrees of freedom acting on H_0 . If you have reason to believe that the external Hamiltonian can be treated classically, then eq. (2.1) follows in a straightforward manner. 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

$$H_0 |n\rangle = E_n |n\rangle. \quad (2.2)$$

The state of the system can be expressed as a superposition of these eigenstates:

$$|\psi(t)\rangle = \sum_n c_n(t) |n\rangle \quad (2.3)$$

The TDSE can be used to find an equation of motion for the expansion coefficients

$$c_k(t) = \langle k | \psi(t) \rangle \quad (2.4)$$

Starting with

$$\frac{\partial |\psi\rangle}{\partial t} = \frac{-i}{\hbar} H |\psi\rangle \quad (2.5)$$

$$\frac{\partial c_k(t)}{\partial t} = -\frac{i}{\hbar} \langle k | H | \psi(t) \rangle \quad (2.6)$$

$$\text{inserting } \sum_n |n\rangle \langle n| = 1 \quad = -\frac{i}{\hbar} \sum_n \langle k | H | n \rangle c_n(t) \quad (2.7)$$

substituting eq. (2.1) we have:

$$\begin{aligned}\frac{\partial c_k(t)}{\partial t} &= -\frac{i}{\hbar} \sum_n \langle k | (H_0 + V(t)) | n \rangle c_n(t) \\ &= -\frac{i}{\hbar} \sum_n [E_n \delta_{kn} + V_{kn}(t)] c_n(t)\end{aligned}\quad (2.8)$$

or,

$$\frac{\partial c_k(t)}{\partial t} + \frac{i}{\hbar} E_k c_k(t) = -\frac{i}{\hbar} \sum_n V_{kn}(t) c_n(t). \quad (2.9)$$

If we make a substitution

$$c_m(t) = e^{-iE_m t/\hbar} b_m(t), \quad (2.10)$$

which defines a slightly different expansion coefficient, we can simplify considerably. Notice that $|b_k(t)|^2 = |c_k(t)|^2$. Also, $b_k(0) = c_k(0)$. In practice what we are doing is pulling out the “trivial” part of the time-evolution, the time-evolving phase factor for state m . The reasons will become clear later when we discuss the interaction picture. It is easy to calculate $b_k(t)$ and then add in the extra oscillatory term at the end. Now eq. (2.9) becomes

$$e^{-iE_k t/\hbar} \frac{\partial b_k}{\partial t} = -\frac{i}{\hbar} \sum_n V_{kn}(t) e^{-iE_n t/\hbar} b_n(t) \quad (2.11)$$

or

$$\boxed{i\hbar \frac{\partial b_k}{\partial t} = \sum_n V_{kn}(t) e^{-i\omega_{nk}t} b_n(t)} \quad (2.12)$$

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

As an example of the use of these equations, let's describe what happens when you drive a two-level system with an oscillating potential.

$$V(t) = V \cos \omega t = V f(t) \quad (2.13)$$

Note: This is what you expect for an electromagnetic field interacting with charged particles, i.e. dipole transitions. In a simple sense, the electric field is

$$\bar{E}(t) = \bar{E}_0 \cos \omega t \quad (2.14)$$

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

$$\bar{F} = q \bar{E} \quad (2.15)$$

which is the gradient of the potential

$$F_x = -\frac{\partial V}{\partial x} = qE_x \Rightarrow V = -qE_x x \quad (2.16)$$

qx is just the x component of the dipole moment μ . So matrix elements in V look like:

$$\langle k | V(t) | \ell \rangle = -qE_x \langle k | x | \ell \rangle \cos \omega t \quad (2.17)$$

More generally,

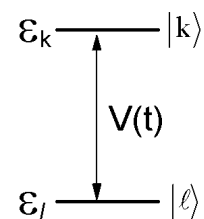
$$V = -\bar{E} \cdot \bar{\mu}. \quad (2.18)$$

We'll look at this a bit more carefully later.

So,

$$\begin{aligned} V(t) &= V \cos \omega t = -\bar{E}_0 \cdot \bar{\mu} \cos \omega t \\ V_{k\ell}(t) &= V_{k\ell} \cos \omega t = -\bar{E}_0 \cdot \bar{\mu}_{k\ell} \cos \omega t \end{aligned} \quad (2.19)$$

We will now couple our two states $|k\rangle$ and $|\ell\rangle$ 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:

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} b_k(t) &= \sum_n b_n(t) V_{kn}(t) e^{-i\omega_{nk}t} \\ &= \sum_n b_n(t) V_{kn} e^{-i\omega_{nk}t} \times \frac{1}{2} (e^{-i\omega t} + e^{+i\omega t}) \end{aligned} \quad (2.20)$$

Or more explicitly

$$\begin{aligned} i\hbar \dot{b}_k &= \frac{1}{2} b_\ell V_{k\ell} \left[e^{i(\omega_{k\ell} - \omega)t} + e^{i(\omega_{k\ell} + \omega)t} \right] + \frac{1}{2} b_k V_{kk} \left[e^{i\omega t} + e^{-i\omega t} \right] \\ i\hbar \dot{b}_\ell &= \frac{1}{2} b_\ell V_{\ell\ell} \left[e^{i\omega t} + e^{-i\omega t} \right] + \frac{1}{2} b_k V_{\ell k} \left[e^{i(\omega_{\ell k} - \omega)t} + e^{i(\omega_{\ell k} + \omega)t} \right] \end{aligned} \quad (2.21)$$

or

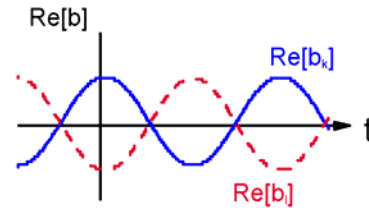
$$\left[e^{-i(\omega_{k\ell} + \omega)t} + e^{-i(\omega_{k\ell} - \omega)t} \right]$$

Two of these terms can be dropped since (for our case) the diagonal matrix elements $V_{ii} = 0$. We also make the **secular approximation** (rotating wave approximation) in which the nonresonant terms are dropped. When $\omega_{k\ell} \approx \omega$, terms like $e^{\pm i\omega t}$ or $e^{i(\omega_{k\ell} + \omega)t}$ oscillate very rapidly (relative to $|V_{k\ell}|^{-1}$) and so don't contribute much to change of c_n . (Remember that $\omega_{k\ell}$ is positive). So we have:

$$\dot{b}_k = \frac{-i}{2\hbar} b_\ell V_{k\ell} e^{i(\omega_{k\ell} - \omega)t} \quad (2.22)$$

$$\dot{b}_\ell = \frac{-i}{2\hbar} b_k V_{\ell k} e^{-i(\omega_{k\ell} - \omega)t} \quad (2.23)$$

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



Now if we differentiate eq. (2.22):

$$\ddot{b}_k = \frac{-i}{2\hbar} \left[\dot{b}_\ell V_{k\ell} e^{i(\omega_{k\ell} - \omega)t} + i(\omega_{k\ell} - \omega) b_\ell V_{k\ell} e^{i(\omega_{k\ell} - \omega)t} \right] \quad (2.24)$$

Rewrite eq. (2.22):

$$b_\ell = \frac{2i\hbar}{V_{k\ell}} \dot{b}_k e^{-i(\omega_{k\ell} - \omega)t} \quad (2.25)$$

and substitute (2.25) and (2.23) into (2.24), we get linear second order equation for b_k .

$$\ddot{b}_k - i(\omega_{k\ell} - \omega)\dot{b}_k + \frac{|V_{k\ell}|^2}{4\hbar^2} b_k = 0 \quad (2.26)$$

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

$$a\ddot{x} + b\dot{x} + cx = 0 \quad (2.27)$$

$$x = e^{-(b/2a)t} (A \cos \mu t + B \sin \mu t) \quad (2.28)$$

$$\mu = \frac{1}{2a} [4ac - b^2]^{1/2}$$

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

$$P_k = |b_k(t)|^2 = \frac{|V_{k\ell}|^2}{|V_{k\ell}|^2 + \hbar^2(\omega_{k\ell} - \omega)^2} \sin^2 \Omega_r t \quad (2.29)$$

Where the Rabi Frequency

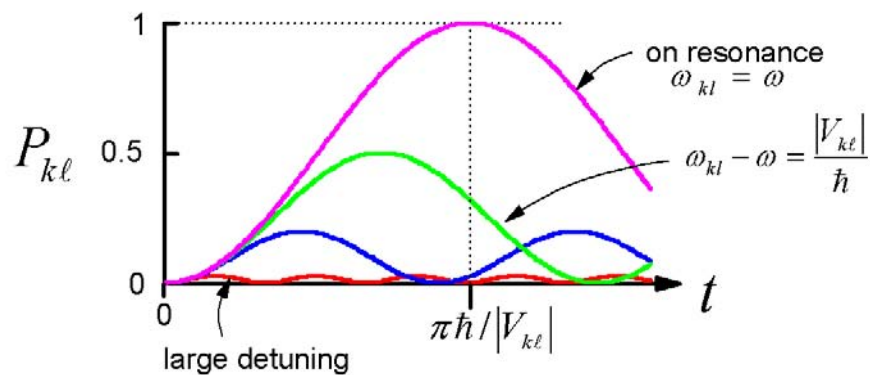
$$\Omega_R = \frac{1}{2\hbar} [|V_{k\ell}|^2 + \hbar^2(\omega_{k\ell} - \omega)^2]^{1/2} \quad (2.30)$$

Also,

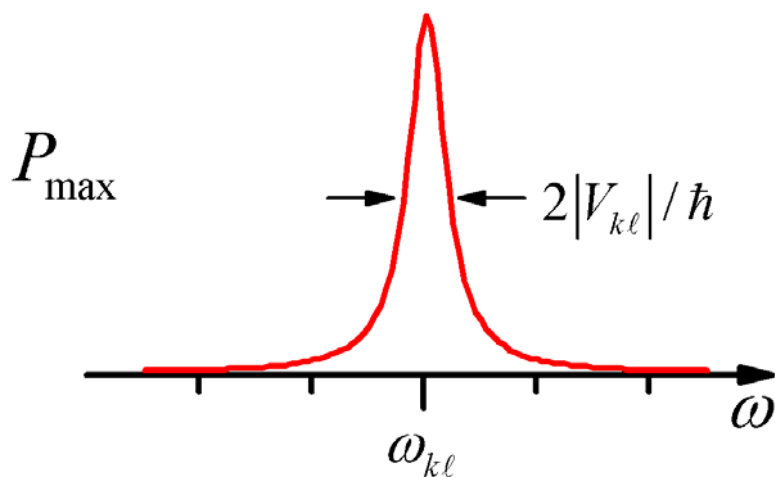
$$P_\ell = 1 - |b_k|^2 \quad (2.31)$$

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 quantum states, creating coherences!]

An important observation is the importance of **resonance** between the driving potential and the energy splitting between states. To get transfer of probability density 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.



The efficiency of driving between l and k states drops off with detuning. Here plotting the maximum value of P_{kl} as a function of frequency:



Readings

This lecture draws from

1. C. Cohen-Tannoudji, B. Diu, and F. Lalöe, *Quantum Mechanics, Vol. 2.* (Wiley-Interscience, Paris, 1977)
2. J. J. Sakurai, *Modern Quantum Mechanics.* (Addison-Wesley, Reading, MA, 1994).

2.2. QUANTUM DYNAMICS

The motion of a particle is described by a complex wavefunction $|\psi(\bar{r}, t)\rangle$ that gives the probability amplitude of finding a particle at point \bar{r} at time t . If we know $|\psi(\bar{r}, t_0)\rangle$, how does it change with time?

$$|\psi(\bar{r}, t_0)\rangle \xrightarrow{?} |\psi(\bar{r}, t)\rangle \quad t > t_0 \quad (2.32)$$

We will use our intuition here (largely based on correspondence to classical mechanics). We are seeking an equation of motion for quantum systems that is equivalent to Newton's (or more accurately Hamilton's) equations for classical systems.

We start by assuming **causality**: $|\psi(t_0)\rangle$ precedes and determines $|\psi(t)\rangle$. So will be deriving a deterministic equation of motion for $|\psi(\bar{r}, t)\rangle$. Also, we assume time is a continuous parameter:

$$\lim_{t \rightarrow t_0} |\psi(t)\rangle = |\psi(t_0)\rangle \quad (2.33)$$

Define an operator that gives time-evolution of system.

$$|\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle \quad (2.34)$$

This “time-displacement operator” or “propagator” is similar to the “space-displacement operator”

$$|\psi(r)\rangle = e^{ik(r-r_0)} |\psi(r_0)\rangle \quad (2.35)$$

which moves a wavefunction in space.

We also say that U does not depend on the particular state of the system $|\psi\rangle$. This is necessary for conservation of probability, i.e. to retain normalization for the system. If

$$|\psi(t_0)\rangle = a_1 |\varphi_1(t_0)\rangle + a_2 |\varphi_2(t_0)\rangle \quad (2.36)$$

then

$$\begin{aligned} |\psi(t)\rangle &= U(t, t_0) |\psi(t_0)\rangle \\ &= U(t, t_0) a_1 |\varphi_1(t_0)\rangle + U(t, t_0) a_2 |\varphi_2(t_0)\rangle \\ &= a_1(t) |\varphi_1\rangle + a_2(t) |\varphi_2\rangle \end{aligned} \quad (2.37)$$

This is a reflection of the importance of linearity in quantum systems. While $|a_i(t)|$ typically not equal to $|a_i(0)|$,

$$\sum_n |a_n(t)|^2 = \sum_n |a_n(t_0)|^2 \quad (2.38)$$

Properties of $U(t,t_0)$

- 1) **Unitary**. Note that for eq. (2.38) to hold and for probability density to be conserved, U must be unitary

$$P = \langle \psi(t) | \psi(t) \rangle = \langle \psi(t_0) | U^\dagger U | \psi(t_0) \rangle \quad (2.39)$$

which holds only if $U^\dagger = U^{-1}$. In fact, this is the reason that equates unitary operators with probability conservation.

- 2) **Time continuity**:

$$U(t,t) = 1. \quad (2.40)$$

- 3) **Composition property**. If we take the system to be deterministic, then it stands to reason that we should get the same wavefunction whether we evolve to a target time in one step ($t_0 \rightarrow t_2$) or multiple steps ($t_0 \rightarrow t_1 \rightarrow t_2$):

$$U(t_2, t_0) = U(t_2, t_1) U(t_1, t_0) \quad (2.41)$$

Note, since U acts to the right, order matters:

$$\begin{aligned} |\psi(t_2)\rangle &= U(t_2, t_1) U(t_1, t_0) |\psi(t_0)\rangle \\ &= U(t_2, t_1) |\psi(t_1)\rangle \end{aligned} \quad (2.42)$$

Equation (2.41) is already very suggestive of an exponential form. Furthermore, since time is continuous and the operator is linear it also suggests what we will see that the time propagator is only dependent on a time interval

$$U(t_1, t_0) = U(t_1 - t_0) \quad (2.43)$$

and

$$U(t_2 - t_0) = U(t_2 - t_1)U(t_1 - t_0) \quad (2.43)$$

- 4) **Time-reversal**. The inverse of the time-propagator is the time reversal operator. From eq. (2.41):

$$U(t, t_0)U(t_0, t) = 1 \quad (2.32)$$

$$\therefore U^{-1}(t, t_0) = U(t_0, t). \quad (2.33)$$

Finding an equation of motion for U

Let's find an equation of motion that describes the time-evolution operator using the change of the system for an infinitesimal time-step, δt : $U(t_0 + \delta t, t_0)$

$$\lim_{\delta t \rightarrow 0} U(t_0 + \delta t, t_0) = 1 \quad (2.34)$$

We expect that for small δt , the difference between $U(t_0, t_0)$ and $U(t_0 + \delta t, t_0)$ will be linear in δt (This is based on analogy to how we think of deterministic motion in classical systems)

$$U(t_0 + \delta t, t_0) = U(t_0, t_0) - i\hat{\Omega}(t_0)\delta t \quad (2.35)$$

We take $\hat{\Omega}$ to be a time-dependent Hermetian operator. We'll see later why the second term must be imaginary. So, now we can write a differential equation for U . We know that

$$U(t + \delta t, t_0) = U(t + \delta t, t)U(t, t_0). \quad (2.36)$$

Knowing the change of U during the period δt allows us to write a differential equation for the time-development of $U(t, t_0)$. The equation of motion for U is

$$\begin{aligned}\frac{dU(t, t_0)}{dt} &= \lim_{\delta t \rightarrow 0} \frac{U(t + \delta t, t_0) - U(t, t_0)}{\delta t} \\ &= \lim_{\delta t \rightarrow 0} \frac{[U(t + \delta t, t) - 1]U(t, t_0)}{\delta t}\end{aligned}\quad (2.37)$$

Where I have substituted eqn. (2.35) in the second step. So we have:

$$\frac{\partial U(t, t_0)}{\partial t} = -i\hat{\Omega}U(t, t_0)\quad (2.38)$$

You can now see that the operator needed a complex argument, because otherwise probability density would not be conserved (it would rise or decay). Rather it oscillates through different states of the system.

We note that $\hat{\Omega}$ has units of frequency. Since (1) quantum mechanics says $E = \hbar\omega$ and (2) in classical mechanics the Hamiltonian generates time-evolution, we write

$$\hat{\Omega} = \frac{\hat{H}}{\hbar}\quad (2.39)$$

Where $\hat{\Omega}$ can be a function of time. Then

$$i\hbar \frac{\partial}{\partial t} U(t, t_0) = \hat{H}U(t, t_0)\quad (2.40)$$

Multiplying from right by $|\psi(t_0)\rangle$ gives the TDSE

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = \hat{H}|\psi\rangle\quad (2.41)$$

We are also interested in the equation of motion for U^\dagger which describes the time-evolution of the conjugate wavefunctions. Following the same approach and recognizing that $U^\dagger(t, t_0)$ acts to the left:

$$\langle\psi(t)| = \langle\psi(t_0)|U^\dagger(t, t_0),\quad (2.42)$$

we get

$$-i\hbar \frac{\partial}{\partial t} U^\dagger(t, t_0) = U^\dagger(t, t_0)\hat{H}\quad (2.43)$$

Evaluating $U(t, t_0)$ for Time-independent Hamiltonian

Direct integration of eqn. (2.40) suggests that U can be expressed as:

$$U(t, t_0) = \exp\left[-\frac{i}{\hbar} H(t - t_0)\right] \quad (2.44)$$

Since H is an operator, we will define this operator through the expansion:

$$\exp\left[-\frac{iH}{\hbar}(t - t_0)\right] = 1 + \frac{-iH}{\hbar}(t - t_0) + \left(\frac{-i}{\hbar}\right)^2 \frac{[H(t - t_0)]^2}{2} + \dots \quad (2.45)$$

Note H commutes at all t . You can confirm the expansion satisfies the equation of motion for U .

To evaluate U for the time-independent Hamiltonian, we expand in a set of eigenkets:

$$H|n\rangle = E_n|n\rangle \quad \sum_n |n\rangle\langle n| = 1 \quad (2.46)$$

So we have

$$\begin{aligned} U(t, t_0) &= \sum_n \exp[-iH(t - t_0)/\hbar] |n\rangle\langle n| \\ &= \sum_n |n\rangle \exp[-iE_n(t - t_0)/\hbar] \langle n| \end{aligned} \quad (2.47)$$

and

$$\begin{aligned} |\psi(t)\rangle &= U(t, t_0) |\psi(t_0)\rangle \\ &= \sum_n |n\rangle \underbrace{\langle n|\psi(t_0)\rangle}_{c_n(t_0)} \exp\left[\frac{-i}{\hbar} E_n(t - t_0)\right] \\ &= \sum_n |n\rangle c_n(t) \end{aligned} \quad (2.48)$$

Expectation values of operators are given by

$$\begin{aligned} \langle A(t) \rangle &= \langle \psi(t) | A | \psi(t) \rangle \\ &= \langle \psi(t_0) | U^\dagger(t, t_0) A U(t, t_0) | \psi(t_0) \rangle \end{aligned} \quad (2.49)$$

For an initial state $|\psi(t_0)\rangle = \sum_n c_n |n\rangle$, we showed in eq. 1.48 that

$$\begin{aligned}
 \langle A \rangle &= \sum_{n,m} c_m^* \langle m|m \rangle e^{+i\omega_m(t-t_0)} \langle m|A|n \rangle e^{-i\omega_n(t-t_0)} \langle n|n \rangle c_n \\
 &= \sum_{n,m} c_m^* c_n A_{mn} e^{-i\omega_{nm}(t-t_0)} \\
 &= \sum_{n,m} c_m^*(t) c_n(t) A_{mn}
 \end{aligned} \tag{2.50}$$

which is $\text{Tr}(\rho(t)A)$. The correlation amplitude $\langle \beta | \psi(t) \rangle$ was given in eq. 1.45.

Evaluating the time-evolution operator: Time-dependent Hamiltonian

At first glance it may seem straightforward to deal with. If H is a function of time, then the formal integration of $i\hbar \partial U / \partial t = HU$ gives

$$U(t, t_0) = \exp \left[\frac{-i}{\hbar} \int_{t_0}^t H(t') dt' \right] \quad (2.51)$$

We would define this exponential as an expansion in a series, and substitute into the equation of motion to confirm it:

$$U(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t H(t') dt' + \frac{1}{2!} \left(\frac{-i}{\hbar} \right)^2 \int_{t_0}^t \int_{t_0}^{t'} dt' dt'' H(t') H(t'') + \dots \quad (2.52)$$

Then if we know the eigenstates of H , we could use eq. (2.46) to express U as

$$U(t, t_0) = \sum_n |n\rangle \exp \left[\frac{-i}{\hbar} \int_{t_0}^t E_j(t') dt' \right] \langle n| \quad (2.53)$$

However, this is dangerous; we are not treating H as an operator. We are assuming that the Hamiltonians at different times commute! $[H(t'), H(t'')] = 0$. It is only the case for special Hamiltonians with a high degree of symmetry, in which the eigenstates have the same symmetry at all times. This holds for instance in the case of a degenerate system, i.e., spin $1/2$ system, with a time-dependent coupling. Generally speaking this is not the case.

Now, let's proceed a bit more carefully assuming that the Hamiltonian at different times does not commute. Integrate

$$\frac{\partial}{\partial t} U(t, t_0) = \frac{-i}{\hbar} H(t) U(t, t_0) \quad (2.54)$$

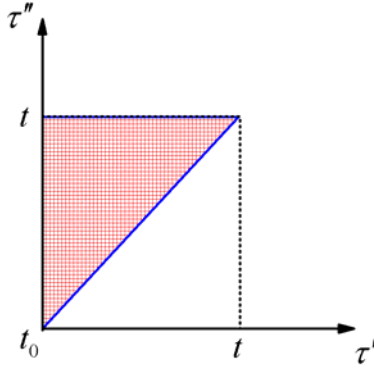
To give:

$$U(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t d\tau H(\tau) U(\tau, t_0) \quad (2.55)$$

This is the solution; however, it's not very practical since $U(t, t_0)$ is a function of itself. But we can solve by iteratively substituting U into itself. First Step:

$$\begin{aligned}
U(t, t_0) &= 1 - \frac{i}{\hbar} \int_{t_0}^t d\tau H(\tau) \left[1 - \frac{i}{\hbar} \int_{t_0}^{\tau} d\tau' H(\tau') U(\tau', t_0) \right] \\
&= 1 + \left(\frac{-i}{\hbar} \right) \int_{t_0}^t d\tau H(\tau) + \left(\frac{-i}{\hbar} \right)^2 \int_{t_0}^t d\tau \int_{t_0}^{\tau} d\tau' H(\tau) H(\tau') U(\tau', t_0)
\end{aligned} \tag{2.56}$$

Note in the last term of this equation, the integration variable τ' precedes τ . Pictorially, the area of integration is

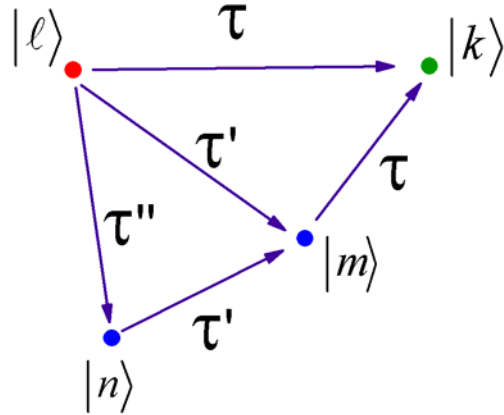


Next Step:

$$\begin{aligned}
U(t, t_0) &= 1 + \left(\frac{-i}{\hbar} \right) \int_{t_0}^t d\tau H(\tau) \\
&\quad + \left(\frac{-i}{\hbar} \right)^2 \int_{t_0}^t d\tau \int_{t_0}^{\tau} d\tau' H(\tau) H(\tau') \\
&\quad + \left(\frac{-i}{\hbar} \right)^3 \int_{t_0}^t d\tau \int_{t_0}^{\tau} d\tau' \int_{t_0}^{\tau'} d\tau'' H(\tau) H(\tau') H(\tau'') U(\tau'', t_0)
\end{aligned} \tag{2.57}$$

From this expansion, you should be aware that there is a time-ordering to the interactions. For the third term, τ'' acts before τ' , which acts before τ : $t_0 \leq \tau'' \leq \tau' \leq \tau \leq t$.

Imagine you are starting in state $|\psi_0\rangle = |\ell\rangle$ and you are working toward a target state $|\psi\rangle = |k\rangle$. The possible paths and associated time variables are:



The expression for U describes all possible paths between initial and final state. Each of these paths interfere in ways dictated by the acquired phase of our eigenstates under the time-dependent Hamiltonian. The solution for U obtained from this iterative substitution is known as the (positive) time-ordered exponential

$$\begin{aligned}
 U(t, t_0) &\equiv \exp_+ \left[\frac{-i}{\hbar} \int_{t_0}^t d\tau H(\tau) \right] \\
 &\equiv \hat{T} \exp \left[\frac{-i}{\hbar} \int_{t_0}^t d\tau H(\tau) \right] \\
 &= 1 + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar} \right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \dots \int_{t_0}^{\tau_1} d\tau_1 H(\tau_n) H(\tau_{n-1}) \dots H(\tau_1)
 \end{aligned} \tag{2.58}$$

(\hat{T} is known as the Tyson time-ordering operator.) In this expression the time-ordering is:

$$\begin{aligned}
 t_0 &\rightarrow \tau_1 \rightarrow \tau_2 \rightarrow \tau_3 \dots \tau_n \rightarrow t \\
 t_0 &\rightarrow \dots \tau'' \rightarrow \tau' \rightarrow \tau
 \end{aligned} \tag{2.59}$$

So, this expression tells you about how a quantum system evolves over a given time interval, and it allows for any possible trajectory from an initial state to a final state through any number of intermediate states. Each term in the expansion accounts for more possible transitions between different intermediate quantum states during this trajectory.

Compare the time-ordered exponential with the traditional expansion of an exponential:

$$1 + \sum_{n=1}^{\infty} \frac{1}{n!} \left(\frac{-i}{\hbar} \right)^n \int_{t_0}^t d\tau_n \dots \int_{t_0}^{\tau_1} d\tau_1 H(\tau_n) H(\tau_{n-1}) \dots H(\tau_1) \tag{2.60}$$

Here the time-variables assume all values, and therefore all orderings for $H(\tau_i)$ are calculated. The areas are normalized by the $n!$ factor. (There are $n!$ time-orderings of the τ_n times.)

We are also interested in the Hermetian conjugate of $U(t, t_0)$, which has the equation of motion in eq. (2.43)

$$\frac{\partial}{\partial t} U^\dagger(t, t_0) = \frac{+i}{\hbar} U^\dagger(t, t_0) H(t) \quad (2.61)$$

If we repeat the method above, remembering that $U^\dagger(t, t_0)$ acts to the left:

$$\langle \psi(t) | = \langle \psi(t_0) | U^\dagger(t, t_0) \quad (2.62)$$

then from

$$U^\dagger(t, t_0) = U^\dagger(t_0, t_0) + \frac{i}{\hbar} \int_{t_0}^t d\tau U^\dagger(t, \tau) H(\tau) \quad (2.63)$$

we obtain a negative-time-ordered exponential:

$$\begin{aligned} U^\dagger(t, t_0) &= \exp_- \left[\frac{i}{\hbar} \int_{t_0}^t d\tau H(\tau) \right] \\ &= 1 + \sum_{n=1}^{\infty} \left(\frac{i}{\hbar} \right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \dots \int_{t_0}^{\tau_2} d\tau_1 H(\tau_1) H(\tau_2) \dots H(\tau_n) \end{aligned} \quad (2.64)$$

Here the $H(\tau_i)$ act to the left.

Readings

This lecture draws from the following:

1. Merzbacher, E. *Quantum Mechanics, 3rd ed.* (Wiley, New York, 1998), Ch. 14.
2. Mukamel, S. *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, New York, 1995), Ch. 2.
3. Sakurai, J. J. *Modern Quantum Mechanics, Revised Edition* (Addison-Wesley, Reading, MA, 1994), Ch. 2.

2.3. SCHRÖDINGER AND HEISENBERG REPRESENTATIONS

The mathematical formulation of the dynamics of a quantum system is not unique. So far we have described the dynamics by propagating the wavefunction, which encodes probability densities. This is known as the Schrödinger representation of quantum mechanics. Ultimately, since we can't measure a wavefunction, we are interested in observables (probability amplitudes associated with Hermetian operators). Looking at a time-evolving expectation value suggests an alternate interpretation of the quantum observable:

$$\begin{aligned}\langle \hat{A}(t) \rangle &= \langle \psi(t) | \hat{A} | \psi(t) \rangle = \langle \psi(0) | U^\dagger \hat{A} U | \psi(0) \rangle \\ &= (\langle \psi(0) | U^\dagger) \hat{A} (U | \psi(0) \rangle) \\ &= \langle \psi(0) | (U^\dagger \hat{A} U) | \psi(0) \rangle\end{aligned}\tag{2.65}$$

The last two expressions here suggest alternate transformation that can describe the dynamics. These have different physical interpretations:

- 1) Transform the eigenvectors: $|\psi(t)\rangle \rightarrow U|\psi\rangle$. Leave operators unchanged.
 - 2) Transform the operators: $\hat{A}(t) \rightarrow U^\dagger \hat{A} U$. Leave eigenvectors unchanged.
- (1) **Schrödinger Picture**: Everything we have done so far. Operators are stationary. Eigenvectors evolve under $U(t, t_0)$.
- (2) **Heisenberg Picture**: Use unitary property of U to transform operators so they evolve in time. The wavefunction is stationary. This is a physically appealing picture, because particles move – there is a time-dependence to position and momentum.

Let's look at time-evolution in these two pictures:

Schrödinger Picture

We have talked about the time-development of $|\psi\rangle$, which is governed by

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = H |\psi\rangle\tag{2.66}$$

in differential form, or alternatively $|\psi(t)\rangle = U(t, t_0)|\psi(t_0)\rangle$ in an integral form. In the Schrödinger picture, for operators typically $\frac{\partial A}{\partial t} = 0$. What about observables? For expectation values of operators $\langle \hat{A}(t) \rangle = \langle \psi(t) | \hat{A} | \psi(t) \rangle$:

$$\begin{aligned}
 i\hbar \frac{\partial}{\partial t} \langle \hat{A}(t) \rangle &= i\hbar \left[\left\langle \psi \left| \hat{A} \left| \frac{\partial \psi}{\partial t} \right. \right\rangle + \left\langle \frac{\partial \psi}{\partial t} \left| \hat{A} \right| \psi \right\rangle + \left\langle \psi \left| \frac{\partial \hat{A}}{\partial t} \right| \psi \right\rangle \right] \\
 &= \langle \psi | \hat{A} H | \psi \rangle - \langle \psi | H \hat{A} | \psi \rangle \\
 &= \langle \psi | [\hat{A}, H] | \psi \rangle \\
 &= \langle [\hat{A}, H] \rangle
 \end{aligned} \tag{2.67}$$

Alternatively, written for the density matrix:

$$\begin{aligned}
 i\hbar \frac{\partial}{\partial t} \langle \hat{A}(t) \rangle &= i\hbar \frac{\partial}{\partial t} \text{Tr}(\hat{A} \rho) \\
 &= i\hbar \text{Tr} \left(\hat{A} \frac{\partial}{\partial t} \rho \right) \\
 &= \text{Tr}(\hat{A} [H, \rho]) \\
 &= \text{Tr}([\hat{A}, H] \rho)
 \end{aligned} \tag{2.68}$$

If \hat{A} is independent of time (as we expect in the Schrödinger picture) and if it commutes with H , it is referred to as a constant of motion.

Heisenberg Picture

From eq. (2.65) we can distinguish the Schrödinger picture from Heisenberg operators:

$$\hat{A}(t) = \langle \psi(t) | \hat{A} | \psi(t) \rangle_S = \langle \psi(t_0) | U^\dagger \hat{A} U | \psi(t_0) \rangle_S = \langle \psi | \hat{A}(t) | \psi \rangle_H \tag{2.69}$$

where the operator is defined as

$$\begin{aligned}
 \hat{A}_H(t) &= U^\dagger(t, t_0) \hat{A}_S U(t, t_0) \\
 \hat{A}_H(t_0) &= \hat{A}_S
 \end{aligned} \tag{2.70}$$

Also, since the wavefunction should be time-independent $\partial|\psi_H\rangle/\partial t=0$, we can relate the Schrödinger and Heisenberg wavefunctions as

$$|\psi_S(t)\rangle = U(t, t_0)|\psi_H\rangle \quad (2.71)$$

So,
$$|\psi_H\rangle = U^\dagger(t, t_0)|\psi_S(t)\rangle = |\psi_S(t_0)\rangle \quad (2.72)$$

In either picture the eigenvalues are preserved:

$$\begin{aligned} \hat{A}|\varphi_i\rangle_S &= a_i|\varphi_i\rangle_S \\ U^\dagger\hat{A}UU^\dagger|\varphi_i\rangle_S &= a_iU^\dagger|\varphi_i\rangle_S \\ \hat{A}_H|\varphi_i\rangle_H &= a_i|\varphi_i\rangle_H \end{aligned} \quad (2.73)$$

The time-evolution of the operators in the Heisenberg picture is:

$$\begin{aligned} \frac{\partial\hat{A}_H}{\partial t} &= \frac{\partial}{\partial t}(U^\dagger\hat{A}_S U) = \frac{\partial U^\dagger}{\partial t}\hat{A}_S U + U^\dagger\hat{A}_S \frac{\partial U}{\partial t} + U^\dagger \frac{\partial\hat{A}_S}{\partial t} U \\ &= \frac{i}{\hbar}U^\dagger H \hat{A}_S U - \frac{i}{\hbar}U^\dagger \hat{A}_S H U + \left(\frac{\partial\hat{A}_S}{\partial t}\right)_H \\ &= \frac{i}{\hbar}H_H \hat{A}_H - \frac{i}{\hbar}\hat{A}_H H_H \\ &= \frac{-i}{\hbar}[\hat{A}, H]_H \end{aligned} \quad (2.74)$$

The result:
$$i\hbar \frac{\partial}{\partial t} \hat{A}_H = [\hat{A}, H]_H \quad (2.75)$$

is known as the Heisenberg equation of motion. Here I have written $H_H = U^\dagger H U$. Generally speaking, for a time-independent Hamiltonian $U = e^{-iHt/\hbar}$, U and H commute, and $H_H = H$. For a time-dependent Hamiltonian, U and H need not commute.

Particle in a potential

Often we want to describe the equations of motion for particles with an arbitrary potential:

$$H = \frac{p^2}{2m} + V(x) \quad (2.76)$$

For which the Heisenberg equation gives:

$$\dot{p} = -\frac{\partial V}{\partial x}. \quad (2.77)$$

$$\dot{x} = \frac{p}{m} \quad (2.78)$$

Here, I've made use of

$$[\hat{x}^n, \hat{p}] = i\hbar n\hat{x}^{n-1} \quad (2.79)$$

$$[\hat{x}, \hat{p}^n] = i\hbar n\hat{p}^{n-1} \quad (2.80)$$

These equations indicate that the position and momentum operators follow equations of motion identical to the classical variables in Hamilton's equations. These do not involve factors of \hbar . Note here that if we integrate eq. (2.78) over a time period t we find:

$$\langle x(t) \rangle = \frac{\langle p \rangle t}{m} + \langle x(0) \rangle \quad (2.81)$$

implying that the expectation value for the position of the particle follows the classical motion. These equations also hold for the expectation values for the position and momentum operators (Ehrenfest's Theorem) and indicate the nature of the classical correspondence. In correspondence to Newton's equation, we see

$$m \frac{\partial^2 \langle x \rangle}{\partial t^2} = -\langle \nabla V \rangle \quad (2.82)$$

THE INTERACTION PICTURE

The interaction picture is a hybrid representation that is useful in solving problems with time-dependent Hamiltonians in which we can partition the Hamiltonian as

$$H(t) = H_0 + V(t) \quad (2.83)$$

H_0 is a Hamiltonian for the degrees of freedom we are interested in, which we treat exactly, and can be (although for us generally won't be) a function of time. $V(t)$ is a time-dependent potential which can be complicated. In the interaction picture we will treat each part of the Hamiltonian in a different representation. We will use the eigenstates of H_0 as a basis set to describe the dynamics induced by $V(t)$, assuming that $V(t)$ is small enough that eigenstates of H_0 are a useful basis to describe H . If H_0 is not a function of time, then there is simple time-dependence to this part of the Hamiltonian, that we may be able to account for easily.

Setting V to zero, we can see that the time evolution of the exact part of the Hamiltonian H_0 is described by

$$\frac{\partial}{\partial t} U_0(t, t_0) = \frac{-i}{\hbar} H_0(t) U_0(t, t_0) \quad (2.84)$$

where, most generally,
$$U_0(t, t_0) = \exp_+ \left[\frac{i}{\hbar} \int_{t_0}^t d\tau H_0(\tau) \right] \quad (2.85)$$

but for a time-independent H_0
$$U_0(t, t_0) = e^{-iH_0(t-t_0)/\hbar} \quad (2.86)$$

We define a wavefunction in the interaction picture $|\psi_I\rangle$ through:

$$|\psi_S(t)\rangle \equiv U_0(t, t_0) |\psi_I(t)\rangle \quad (2.87)$$

or
$$|\psi_I\rangle = U_0^\dagger |\psi_S\rangle \quad (2.88)$$

Effectively the interaction representation defines wavefunctions in such a way that the phase accumulated under $e^{-iH_0 t/\hbar}$ is removed. For small V , these are typically high frequency oscillations relative to the slower amplitude changes in coherences induced by V .

We are after an equation of motion that describes the time-evolution of the interaction picture wave-functions. We begin by substituting eq. (2.87) into the TDSE:

$$i\hbar \frac{\partial}{\partial t} |\psi_S\rangle = H |\psi_S\rangle \quad (2.89)$$

$$\frac{\partial}{\partial t} U_0(t, t_0) |\psi_I\rangle = \frac{-i}{\hbar} H(t) U_0(t, t_0) |\psi_I\rangle$$

$$\frac{\partial U_0}{\partial t} |\psi_I\rangle + U_0 \frac{\partial |\psi_I\rangle}{\partial t} = \frac{-i}{\hbar} (H_0 + V(t)) U_0(t, t_0) |\psi_I\rangle \quad (2.90)$$

$$\cancel{\frac{-i}{\hbar} H_0 U_0 |\psi_I\rangle} + U_0 \frac{\partial |\psi_I\rangle}{\partial t} = \frac{-i}{\hbar} (\cancel{H_0} + V(t)) U_0 |\psi_I\rangle$$

$$\therefore i\hbar \frac{\partial |\psi_I\rangle}{\partial t} = V_I |\psi_I\rangle \quad (2.91)$$

where

$$V_I(t) = U_0^\dagger(t, t_0) V(t) U_0(t, t_0) \quad (2.92)$$

$|\psi_I\rangle$ satisfies the Schrödinger equation with a new Hamiltonian: the interaction picture Hamiltonian, $V_I(t)$, which is the U_0 unitary transformation of $V(t)$. Note: Matrix elements in $V_I = \langle k | V_I | l \rangle = e^{-i\omega_k t} V_{kl}$ where k and l are eigenstates of H_0 .

We can now define a time-evolution operator in the interaction picture:

$$|\psi_I(t)\rangle = U_I(t, t_0) |\psi_I(t_0)\rangle \quad (2.93)$$

where

$$U_I(t, t_0) = \exp_+ \left[\frac{-i}{\hbar} \int_{t_0}^t d\tau V_I(\tau) \right]. \quad (2.94)$$

Now we see that

$$\begin{aligned} |\psi_S(t)\rangle &= U_0(t, t_0) |\psi_I(t)\rangle \\ &= U_0(t, t_0) U_I(t, t_0) |\psi_I(t_0)\rangle \\ &= U_0(t, t_0) U_I(t, t_0) |\psi_S(t_0)\rangle \end{aligned} \quad (2.95)$$

$$\therefore U(t, t_0) = U_0(t, t_0) U_I(t, t_0) \quad (2.96)$$

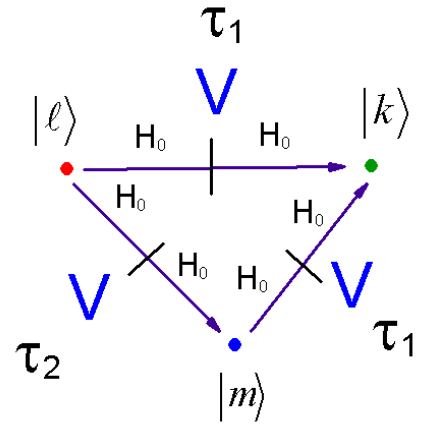
Using the time ordered exponential in eq. (2.94), U can be written as

$$U(t, t_0) = U_0(t, t_0) + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar} \right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \dots \int_{t_0}^{\tau_2} d\tau_1 U_0(t, \tau_n) V(\tau_n) U_0(\tau_n, \tau_{n-1}) \dots U_0(\tau_2, \tau_1) V(\tau_1) U_0(\tau_1, t_0) \quad (2.97)$$

where we have used the composition property of $U(t, t_0)$. The same positive time-ordering applies. Note that the interactions $V(\tau_i)$ are not in the interaction representation here. Rather we used the definition in eq. (2.92) and collected terms.

For transitions between two eigenstates of H_0 (l and k): The system evolves in eigenstates of H_0 during the different time periods, with the time-dependent interactions V driving the transitions between these states. The time-ordered exponential accounts for all possible intermediate pathways.

Also, the time evolution of conjugate wavefunction in the interaction picture is expressed as



$$U^\dagger(t, t_0) = U_I^\dagger(t, t_0) U_0^\dagger(t, t_0) = \exp_- \left[\frac{+i}{\hbar} \int_{t_0}^t d\tau V_I(\tau) \right] \exp_- \left[\frac{+i}{\hbar} \int_{t_0}^t d\tau H_0(\tau) \right] \quad (2.98)$$

or $U_0^\dagger = e^{iH(t-t_0)/\hbar}$ when H_0 is independent of time.

The expectation value of an operator is:

$$\begin{aligned} \langle \hat{A}(t) \rangle &= \langle \psi(t) | \hat{A} | \psi(t) \rangle \\ &= \langle \psi(t_0) | U^\dagger(t, t_0) \hat{A} U(t, t_0) | \psi(t_0) \rangle \\ &= \langle \psi(t_0) | U_I^\dagger U_0^\dagger \hat{A} U_0 U_I | \psi(t_0) \rangle \\ &= \langle \psi_I(t) | \hat{A}_I | \psi_I(t) \rangle \end{aligned} \quad (2.99)$$

$$\text{where} \quad A_I \equiv U_0^\dagger A_S U_0 \quad (2.100)$$

Differentiating A_I gives:

$$\frac{\partial}{\partial t} \hat{A}_I = \frac{i}{\hbar} [H_0, \hat{A}_I] \quad (2.101)$$

also,
$$\frac{\partial}{\partial t} |\psi_I\rangle = \frac{-i}{\hbar} V_I(t) |\psi_I\rangle \quad (2.102)$$

Notice that the interaction representation is a partition between the Schrödinger and Heisenberg representations. Wavefunctions evolve under V_I , while operators evolve under H_0 .

$$\begin{array}{ll} \text{For } H_0 = 0, V(t) = H \Rightarrow \frac{\partial \hat{A}}{\partial t} = 0; \quad \frac{\partial}{\partial t} |\psi_S\rangle = \frac{-i}{\hbar} H |\psi_S\rangle & \text{Schrödinger} \\ \text{For } H_0 = H, V(t) = 0 \Rightarrow \frac{\partial \hat{A}}{\partial t} = \frac{i}{\hbar} [H, \hat{A}]; \quad \frac{\partial \psi}{\partial t} = 0 & \text{Heisenberg} \end{array} \quad (2.103)$$

The relationship between $U(t, t_0)$ and $b_n(t)$

For problems in which we partition a time-dependent Hamiltonian,

$$H = H_0 + V(t) \quad (2.104)$$

H_0 is the time-independent exact zero-order Hamiltonian and $V(t)$ is a time-dependent potential. We know the eigenkets and eigenvalues of H_0 :

$$H_0 |n\rangle = E_n |n\rangle \quad (2.105)$$

and we can describe the state of the system as a superposition of these eigenstates:

$$|\psi(t)\rangle = \sum_n c_n(t) |n\rangle \quad (2.106)$$

The expansion coefficients $c_k(t)$ are given by

$$c_k(t) = \langle k | \psi(t) \rangle = \langle k | U(t, t_0) | \psi(t_0) \rangle \quad (2.107)$$

Alternatively we can express the expansion coefficients in terms of the interaction picture wavefunctions

$$b_k(t) = \langle k | \psi_I(t) \rangle = \langle k | U_I | \psi(t_0) \rangle \quad (2.108)$$

(This notation follows Cohen-Tannoudji.) Notice

$$\begin{aligned} c_k(t) &= \langle k | U_0 U_I | \psi(t_0) \rangle \\ &= e^{-i\omega_k t} \langle k | U_I | \psi(t_0) \rangle \\ &= e^{-i\omega_k t} b_k(t) \end{aligned} \quad (2.109)$$

This is the same identity we used earlier to derive the coupled differential equations that describe the change in the time-evolving amplitude of the eigenstates:

$$i\hbar \frac{\partial b_k}{\partial t} = \sum_n V_{kn}(t) e^{-i\omega_{nk}t} b_n(t) \quad (2.110)$$

So, b_k is the expansion coefficient of the interaction picture wavefunctions. Remember

$|b_k(t)|^2 = |c_k(t)|^2$ and $b_k(0) = c_k(0)$. If necessary we can calculate $b_k(t)$ and then add in the extra oscillatory term at the end.

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 $V(t)$:

$$|\psi_I(t)\rangle = \sum_n b_n(t)|n\rangle \quad (2.111)$$

- 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:

$$b_k = \langle k|U_I(t, t_0)|\psi(t_0)\rangle \quad (2.112)$$

where

$$U_I(t, t_0) = \exp_+ \left[\frac{-i}{\hbar} \int_{t_0}^t V_I(\tau) d\tau \right] \quad (2.113)$$

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 $V(t)$.

$$P_k(t) = |b_k(t)|^2 \quad b_k(t) = \langle k|U_I(t, t_0)|\ell\rangle \quad (2.114)$$

$$b_k(t) = \left\langle k \left| \exp_+ \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau V_I(\tau) \right] \right| \ell \right\rangle \quad (2.115)$$

$$\begin{aligned}
b_k(t) = \langle k | \ell \rangle - \frac{i}{\hbar} \int_{t_0}^t d\tau \langle k | V_I(\tau) | \ell \rangle \\
+ \left(\frac{-i}{\hbar} \right)^2 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \langle k | V_I(\tau_2) V_I(\tau_1) | \ell \rangle + \dots
\end{aligned} \tag{2.116}$$

using
$$\langle k | V_I(t) | \ell \rangle = \langle k | U_0^\dagger V(t) U_0 | \ell \rangle = e^{-i\omega_{k\ell}t} V_{k\ell}(t) \tag{2.117}$$

So,
$$b_k(t) = \delta_{k\ell} - \frac{i}{\hbar} \int_{t_0}^t d\tau_1 e^{-i\omega_{k\ell}\tau_1} V_{k\ell}(\tau_1) \tag{2.118}$$
 “first order”

$$+ \sum_m \left(\frac{-i}{\hbar} \right)^2 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 e^{-i\omega_{mk}\tau_2} V_{km}(\tau_2) e^{-i\omega_{\ell m}\tau_1} V_{m\ell}(\tau_1) + \dots \tag{2.119}$$

“second order”

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 $|k\rangle$:

$$\frac{\partial}{\partial t} b_k = \frac{-i}{\hbar} e^{-i\omega_{k\ell}t} V_{k\ell}(t) b_\ell(0) \tag{2.120}$$

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,

$$|\psi_0\rangle = \sum_n b_n(0) |n\rangle \text{ and } b_k(t) = \sum_n b_n(0) \langle k | U_I | n \rangle. \tag{2.121}$$

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

$$P_k(t) = |c_k(t)|^2 = |b_k(t)|^2 = \left| \sum_n \langle k | b_n(t) | n \rangle \right|^2 \quad (2.122)$$

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 $\omega_{k\ell}$.

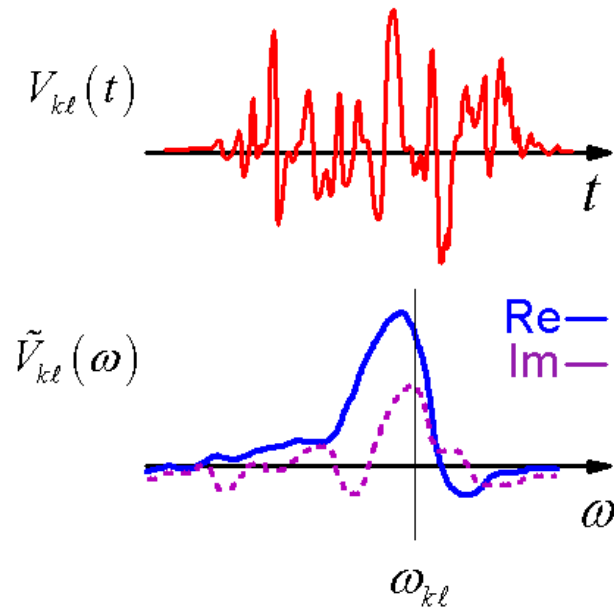
$$b_k(t) = -\frac{i}{\hbar} \int_{-\infty}^{+\infty} d\tau e^{-i\omega_{k\ell}\tau} V_{k\ell}(\tau) \quad (2.123)$$

If the Fourier transform is defined as

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

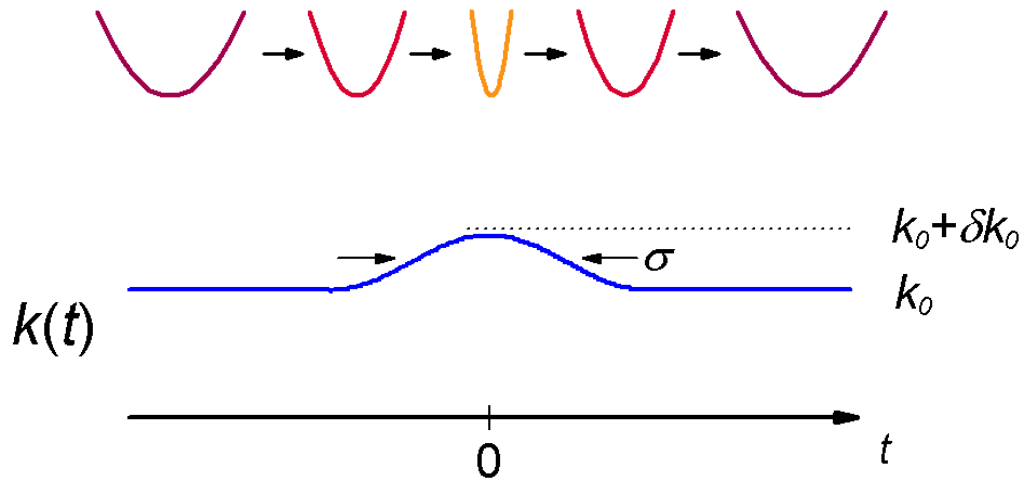
then

$$P_{k\ell} = |\tilde{V}(\omega_{k\ell})|^2. \quad (2.125)$$



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.



First write the Hamiltonian:

$$H(t) = T + V(t) = \frac{p^2}{2m} + \frac{1}{2}k(t)x^2 \quad (2.126)$$

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

$$k(t) = k_0 + \delta k(t) \quad k_0 = m\Omega^2 \quad \delta k(t) = \delta k_0 \exp\left(-\frac{(t-t_0)^2}{2\sigma^2}\right) \quad (2.127)$$

$$H = \underbrace{\frac{p^2}{2m} + \frac{1}{2}k_0 x^2}_{H_0} + \underbrace{\frac{1}{2}\delta k_0 x^2 \exp\left(-\frac{(t-t_0)^2}{2\sigma^2}\right)}_{V(t)} \quad (2.128)$$

$$H_0 |n\rangle = E_n |n\rangle \quad H_0 = \hbar\Omega \left(a^\dagger a + \frac{1}{2} \right) \quad E_n = \hbar\Omega \left(n + \frac{1}{2} \right) \quad (2.129)$$

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 $n \neq 0$:

$$b_n(t) = \frac{-i}{2\hbar} \int_{t_0}^t d\tau V_{n0}(\tau) e^{i\omega_{n0}\tau} \quad (2.130)$$

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

$$b_n(t) = \frac{-i}{2\hbar} \delta k_0 \langle n|x^2|0\rangle \int_{-\infty}^{+\infty} d\tau e^{in\Omega\tau} e^{-\tau^2/2\sigma^2} \quad (2.131)$$

So,

$$b_n(t) = \frac{-i}{2\hbar} \delta k_0 \sqrt{2\pi}\sigma \langle n|x^2|0\rangle e^{-n^2\sigma^2\Omega^2/2} \quad (2.132)$$

Here we used:

What about the matrix element?

$$x^2 = \frac{\hbar}{2m\Omega} (a + a^\dagger)^2 = \frac{\hbar}{2m\Omega} (aa + a^\dagger a + aa^\dagger + a^\dagger a^\dagger) \quad (2.133)$$

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,

$$\langle 2|x^2|0\rangle = \sqrt{2} \frac{\hbar}{2m\Omega} \quad (2.134)$$

So,

$$b_2 = \frac{-i\sqrt{\pi}\delta k_0\sigma}{2m\Omega} e^{-2\sigma^2\Omega^2} \quad (2.135)$$

and

$$P_2 = |b_2|^2 = \frac{\pi\delta k_0^2\sigma^2}{2m^2\Omega^2} e^{-4\sigma^2\Omega^2} = \sigma^2\Omega^2 \frac{\pi}{2} \left(\frac{\delta k_0^2}{k_0^2} \right) e^{-4\sigma^2\Omega^2} \quad (2.136)$$

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

$$\sigma \ll \frac{1}{\Omega} \quad (2.137)$$

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

$$\sigma^2 \Omega^2 \frac{\pi}{2} \left(\frac{\delta k_0^2}{k_0^2} \right) \ll 1 \quad (2.138)$$

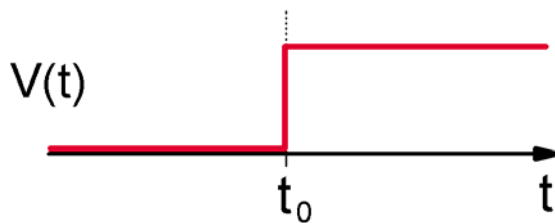
Generally, the perturbation $\delta k(t)$ must be small compared to k_0 , i.e. $|H_0| \gg |V|$, but it should also work well for the impulsive shock limit ($\sigma \Omega \ll 1$).

FIRST-ORDER PERTURBATION THEORY

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

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

$$b_k = \delta_{k\ell} - \frac{i}{\hbar} \int_{t_0}^t d\tau e^{i\omega_{k\ell}(\tau-t_0)} V_{k\ell}(\tau) \quad (2.139)$$

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

$$b_k = -\frac{i}{\hbar} V_{k\ell} \int_0^t d\tau e^{i\omega_{k\ell}\tau} \quad (2.140)$$

$$= -\frac{V_{k\ell}}{E_k - E_\ell} [\exp(i\omega_{k\ell}t) - 1] \quad (2.141)$$

$$= -\frac{2iV_{k\ell} e^{i\omega_{k\ell}t/2}}{E_k - E_\ell} \sin(\omega_{k\ell}t/2) \quad (2.142)$$

Where I used $e^{i\theta} - 1 = 2i e^{i\theta/2} \sin(\theta/2)$. Now

$$P_k = |b_k|^2 = \frac{4|V_{k\ell}|^2}{|E_k - E_\ell|^2} \sin^2 \frac{1}{2} \omega_{k\ell}t \quad (2.143)$$

Writing this as we did in Lecture 1:

$$P_k = \frac{V^2}{\Delta^2} \sin^2(\Delta t / \hbar) \quad (2.144)$$

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

$$P_k = \frac{V^2}{V^2 + \Delta^2} \sin^2\left(\sqrt{\Delta^2 + V^2} t / \hbar\right) \quad (2.145)$$

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

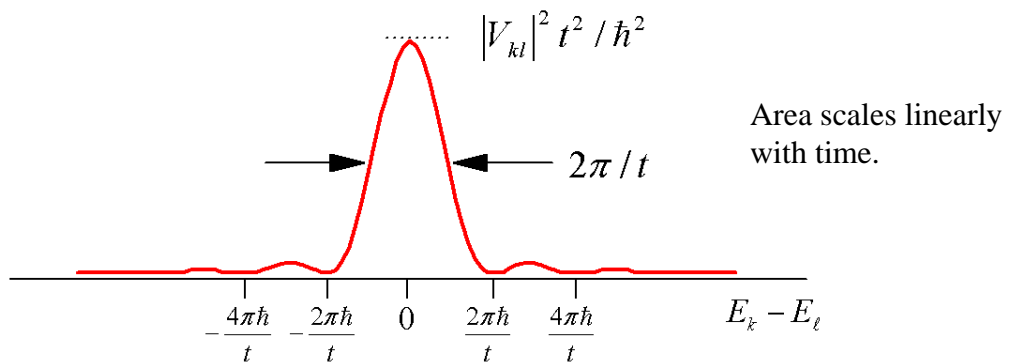
We can also write the first-order result as

$$P_k = \frac{V^2 t^2}{\hbar^2} \text{sinc}^2(\Delta t / 2\hbar) \quad (2.146)$$

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

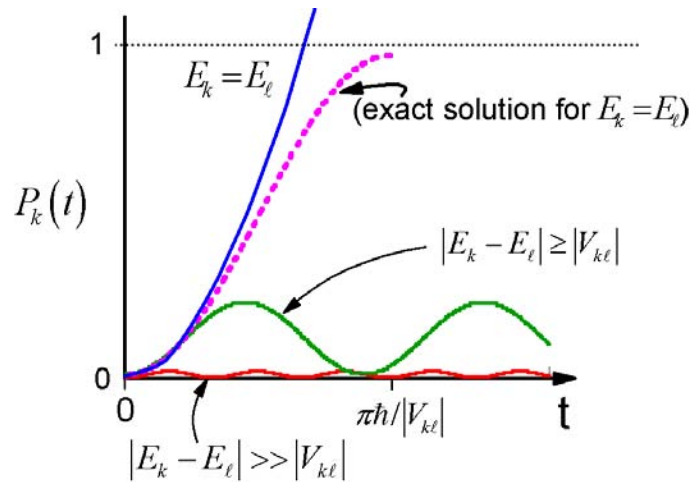
$$\lim_{\Delta \rightarrow 0} P_k = V^2 t^2 / \hbar^2 \quad (2.147)$$

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



Since the energy spread of states to which transfer is efficient scales approximately as $E_k - E_\ell < 2\pi\hbar/t$, 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 uncertainty 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:

$$\lim_{t \rightarrow \infty} \frac{\sin^2(ax/2)}{ax^2} = \frac{\pi}{2} \delta(x) \quad (2.148)$$

$$\lim_{t \rightarrow \infty} P_k(t) = \frac{2\pi |V_{k\ell}|^2}{\hbar} \delta(E_k - E_\ell) t \quad (2.149)$$

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 kinetics:

$$w_k(t) = \frac{\partial P_k(t)}{\partial t} = \frac{2\pi |V_{k\ell}|^2}{\hbar} \delta(E_k - E_\ell) \quad (2.150)$$

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

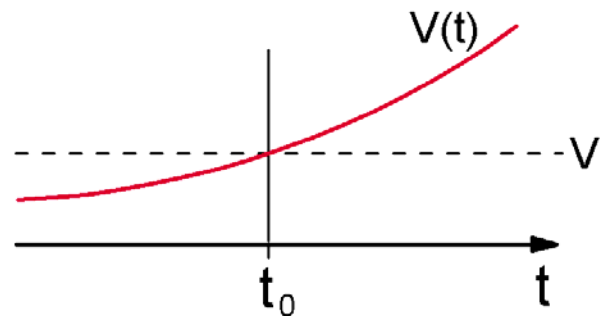
Our perturbation was applied suddenly at $t > t_0$ (step function)

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

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 η is a small positive number. η^{-1} is the effective turn-on time of the perturbation.

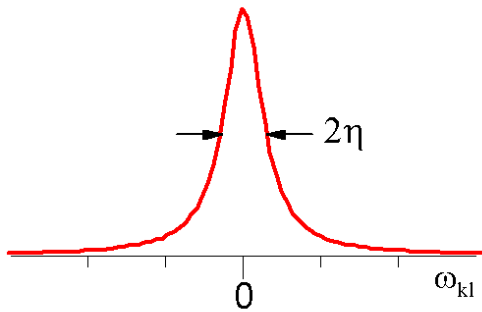
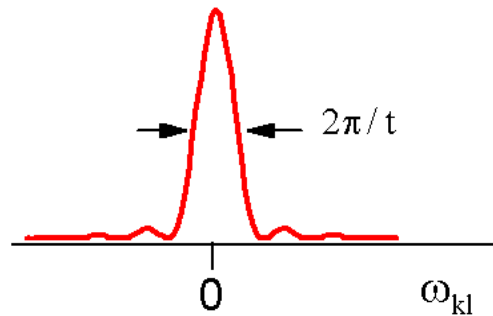
The system is prepared in state $|\ell\rangle$ at $t = -\infty$. Find $P_k(t)$.

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

$$\begin{aligned} b_k &= \frac{-iV_{k\ell}}{\hbar} \frac{\exp[\eta t + i\omega_{k\ell}t]}{\eta + i\omega_{k\ell}} \\ &= V_{k\ell} \frac{\exp[\eta t + i(E_k - E_\ell)t / \hbar]}{E_k - E_\ell + i\eta\hbar} \end{aligned}$$

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

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:

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

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

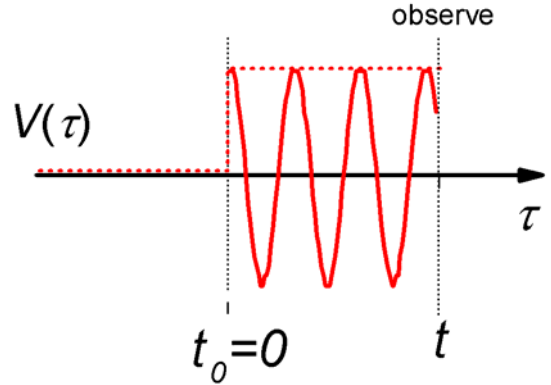
$$\lim_{\eta \rightarrow 0} \frac{\eta}{\eta^2 + \omega_{kl}^2} = \pi \delta(\omega_{kl})$$

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

We get Fermi's Golden Rule—independent 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 ℓ and k :



$$V(t) = V \cos \omega t = -\mu E_0 \cos \omega t \quad (2.151)$$

$$\begin{aligned} V_{k\ell}(t) &= V_{k\ell} \cos \omega t \\ &= \frac{V_{k\ell}}{2} [e^{i\omega t} + e^{-i\omega t}] \end{aligned} \quad (2.152)$$

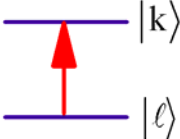
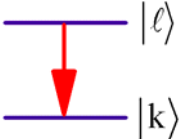
To first order, we have:

$$\begin{aligned} b_k &= \langle k | \psi_I(t) \rangle = \frac{-i}{\hbar} \int_{t_0}^t d\tau V_{k\ell}(\tau) e^{i\omega_{k\ell}\tau} \\ &= \frac{-iV_{k\ell}}{2\hbar} \int_0^t d\tau [e^{i(\omega_{k\ell}+\omega)\tau} - e^{i(\omega_{k\ell}-\omega)\tau}] \quad \text{setting } t_0 \rightarrow 0 \quad (2.153) \\ &= \frac{-V_{k\ell}}{2\hbar} \left[\frac{e^{i(\omega_{k\ell}+\omega)t} - 1}{\omega_{k\ell} + \omega} + \frac{e^{i(\omega_{k\ell}-\omega)t} - 1}{\omega_{k\ell} - \omega} \right] \end{aligned}$$

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

$$b_k = \frac{-iV_{k\ell}}{\hbar} \left[\frac{e^{i(\omega_{k\ell}-\omega)t/2} \sin[(\omega_{k\ell}-\omega)t/2]}{\omega_{k\ell}-\omega} + \frac{e^{i(\omega_{k\ell}+\omega)t/2} \sin[(\omega_{k\ell}+\omega)t/2]}{\omega_{k\ell}+\omega} \right] \quad (2.154)$$

Notice that these terms are only significant when $\omega \approx \omega_{k\ell}$. As we learned before, resonance is required to gain significant transfer of amplitude.

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

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

$$P_{k\ell} = |b_k|^2 = \frac{|V_{k\ell}|^2}{\hbar^2 (\omega_{k\ell} - \omega)^2} \sin^2 \left[\frac{1}{2} (\omega_{k\ell} - \omega) t \right] \quad (2.155)$$

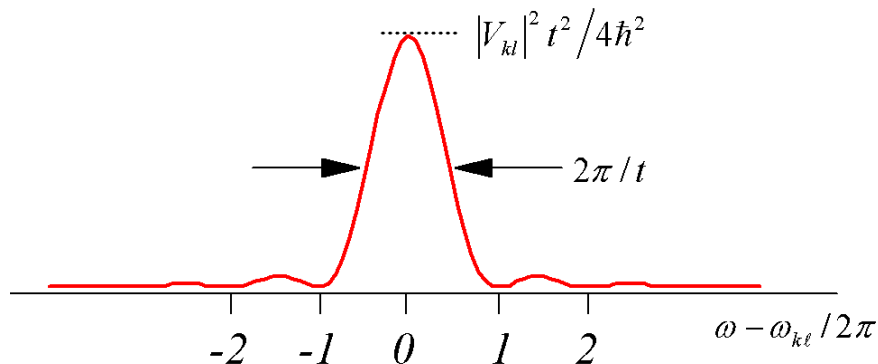
or

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

We can compare this with the exact expression:

$$P_{k\ell} = |b_k|^2 = \frac{|V_{k\ell}|^2}{\hbar^2 (\omega_{k\ell} - \omega)^2 + |V_{k\ell}|^2} \sin^2 \left[\frac{1}{2\hbar} \sqrt{|V_{k\ell}|^2 + (\omega_{k\ell} - \omega)^2} t \right] \quad (2.156)$$

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

$$\lim_{\Delta\omega \rightarrow 0} P_k(t) = \frac{|V_{k\ell}|^2}{4\hbar^2} t^2 \quad (2.157)$$

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

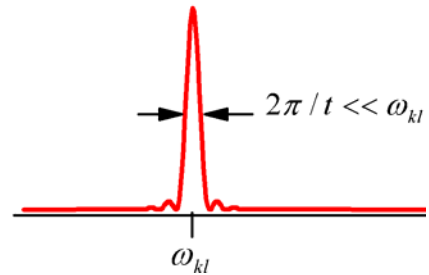
$$t \ll \frac{2\hbar}{V_{k\ell}} \quad (2.158)$$

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.

$$t > \frac{1}{\omega} \approx \frac{1}{\omega_{k\ell}} \quad (2.159)$$

These relationships imply that

$$V_{k\ell} \ll \hbar\omega_{k\ell} \quad (2.160)$$



Adiabatic Harmonic Perturbation

What happens if we slowly turn on the harmonic interaction?

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

$$\begin{aligned} b_k &= \frac{-i}{\hbar} \int_{-\infty}^t d\tau V_{k\ell} e^{i\omega_{k\ell}\tau + \eta\tau} \left[\frac{e^{i\omega\tau} + e^{-i\omega\tau}}{2} \right] \\ &= \frac{V_{k\ell}}{2\hbar} e^{\eta t} \left[\frac{e^{i(\omega_{k\ell} + \omega)t}}{-(\omega_{k\ell} + \omega) + i\eta} + \frac{e^{i(\omega_{k\ell} - \omega)t}}{-(\omega_{k\ell} - \omega) + i\eta} \right] \end{aligned}$$

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

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

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 $\eta \rightarrow 0$. We will calculate the rate of transitions $w_{k\ell} = \partial P_k / \partial t$. 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) \rightarrow resonances sharpen.

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

2.5 FERMI'S GOLDEN RULE

The transition rate and probability of observing the system in a state $|k\rangle$ after applying a perturbation to $|\ell\rangle$ from the constant first-order perturbation doesn't allow for the feedback between quantum states, so it turns out to be most useful in cases where we are interested just the rate of leaving a state. This question shows up commonly when we calculate the transition probability not to an individual eigenstate, but a distribution of eigenstates. Often the set of eigenstates form a continuum of accepting states, for instance, vibrational relaxation or ionization.

Transfer to a set of continuum (or bath) states forms the basis for describing irreversible relaxation. You can think of the material Hamiltonian for our problem being partitioned into two portions, $H = H_S + H_B + V_{SB}(t)$, where you are interested in the loss of amplitude in the H_S states as it leaks into H_B . Qualitatively, you expect deterministic, oscillatory feedback between discrete quantum states. However, the amplitude of one discrete state coupled to a continuum will decay due to destructive interferences between the oscillating frequencies for each member of the continuum.

So, using the same ideas as before, let's calculate the transition probability from $|\ell\rangle$ to a distribution of final states: \overline{P}_k .

$P_k = |b_k|^2$ Probability of observing amplitude in discrete eigenstate of H_0

$\rho(E_k)$: Density of states—units in $1/E_k$, describes distribution of final states—all eigenstates of H_0

If we start in a state $|\ell\rangle$, the total transition probability is a sum of probabilities

$$\overline{P}_k = \sum_k P_k . \quad (2.161)$$

We are just interested in the rate of leaving $|\ell\rangle$ and occupying any state $|k\rangle$ or for a continuous distribution:



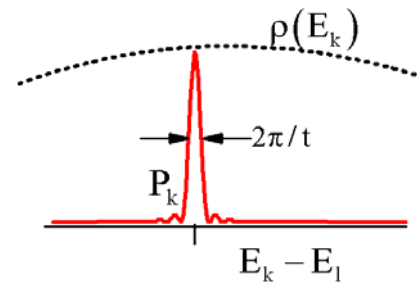
$$\bar{P}_k = \int dE_k \rho(E_k) P_k \quad (2.162)$$

For a constant perturbation:

$$\bar{P}_k = \int dE_k \rho(E_k) 4|V_{k\ell}|^2 \frac{\sin^2((E_k - E_\ell)t / 2\hbar)}{|E_k - E_\ell|^2} \quad (2.163)$$

Now, let's make two assumptions to evaluate this expression:

- 1) $\rho(E_k)$ varies slowly with frequency and there is a continuum of final states. (By slow what we are saying is that the observation point t is relatively long).
- 2) The matrix element $V_{k\ell}$ is invariant across the final states.



These assumptions allow those variables to be factored out of integral

$$\bar{P}_k = \rho |V_{k\ell}|^2 \int_{-\infty}^{+\infty} dE_k 4 \frac{\sin^2((E_k - E_\ell)t / 2\hbar)}{(E_k - E_\ell)^2} \quad (2.164)$$

Here, we have chosen the limits $-\infty \rightarrow +\infty$ since $\rho(E_k)$ is broad relative to P_k . Using the identity

$$\int_{-\infty}^{+\infty} d\Delta \frac{\sin^2 a\Delta}{\Delta^2} = a\pi \quad (2.165)$$

with $a = t / \hbar$ we have

$$\bar{P}_k = \frac{2\pi}{\hbar} \rho |V_{k\ell}|^2 t \quad (2.166)$$

The total transition probability is linearly proportional to time. For relaxation processes, we will be concerned with the transition rate, $\bar{w}_{k\ell}$:

$$\begin{aligned}\bar{w}_{k\ell} &= \frac{\partial \bar{P}_{k\ell}}{\partial t} \\ \bar{w}_{k\ell} &= \frac{2\pi}{\hbar} \rho |V_{k\ell}|^2\end{aligned}\tag{2.167}$$

Remember that P_k is centered sharply at $E_k = E_\ell$. So although ρ is a constant, we usually write eq. (2.167) in terms of $\rho(E_k = E_\ell)$ or more commonly in terms of $\delta(E_k - E_\ell)$:

$$\bar{w}_{k\ell} = \frac{2\pi}{\hbar} \rho(E_k = E_\ell) |V_{k\ell}|^2\tag{2.168}$$

$$w_{k\ell} = \frac{2\pi}{\hbar} |V_{k\ell}|^2 \delta(E_k - E_\ell) \quad \bar{w}_{k\ell} = \int dE_k \rho(E_k) w_{k\ell}\tag{2.169}$$

This expression is known as Fermi's Golden Rule. Note the rates are independent of time. As we will see going forward, this first-order perturbation theory expression involving the matrix element squared and the density of states is very common in the calculation of chemical rate processes.

Range of validity

For discrete states we saw that the first order expression held for $|V_{k\ell}| \ll \hbar\omega_{k\ell}$, and for times such that P_k never varies from initial values.

$$P_k = \bar{w}_{k\ell} (t - t_0) \quad t \ll \frac{1}{\bar{w}_{k\ell}}\tag{2.170}$$

However, transition probability must also be sharp compared to $\rho(E_k)$, which implies

$$t \gg \hbar / \Delta E_k\tag{2.171}$$

So, this expression is useful where

$$\Delta E \gg \bar{w}_{k\ell} \hbar$$

$$\Delta\omega_k \gg \bar{w}_{k\ell}$$

