

2. TIME-EVOLUTION OPERATOR

Dynamical processes in quantum mechanics are described by a Hamiltonian that depends on time. Naturally the question arises how do we deal with a time-dependent Hamiltonian? In principle, the time-dependent Schrödinger equation can be directly integrated choosing a basis set that spans the space of interest. Using a potential energy surface, one can propagate the system forward in small time-steps and follow the evolution of the complex amplitudes in the basis states. In practice even this is impossible for more than a handful of atoms, when you treat all degrees of freedom quantum mechanically. However, the mathematical complexity of solving the time-dependent Schrödinger equation for most molecular systems makes it impossible to obtain exact analytical solutions. We are thus forced to seek numerical solutions based on perturbation or approximation methods that will reduce the complexity. Among these methods, time-dependent perturbation theory is the most widely used approach for calculations in spectroscopy, relaxation, and other rate processes. In this section we will work on classifying approximation methods and work out the details of time-dependent perturbation theory.

2.1. Time-Evolution Operator

Let's start at the beginning by obtaining the equation of motion that describes the wavefunction and its time evolution through the time propagator. We are seeking equations of motion for quantum systems that are equivalent to Newton's—or more accurately Hamilton's—equations for classical systems. The question is, if we know the wavefunction at time t_0 $|\psi(\vec{r}, t_0)\rangle$, how does it change with time? How do we determine $|\psi(\vec{r}, t)\rangle$ for some later time $t > t_0$? We will use our intuition here, based largely on correspondence to classical mechanics). To keep notation to a minimum, in the following discussion we will not explicitly show the spatial dependence of wavefunction.

We start by assuming *causality*: $|\psi(t_0)\rangle$ precedes and determines $|\psi(t)\rangle$, which is crucial for deriving a deterministic equation of motion. Also, as usual, we assume time is a continuous variable:

$$\lim_{t \rightarrow t_0} |\psi(t)\rangle = |\psi(t_0)\rangle \quad (2.1)$$

Now define an “time-displacement operator” or “propagator” that acts on the wavefunction to the right and thereby propagates the system forward in time:

$$|\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle \quad (2.2)$$

We also know that the operator U cannot be dependent on the state of the system $|\psi\rangle$. This is necessary for conservation of probability, i.e., to retain normalization for the system. If

$$|\psi(t_0)\rangle = a_1 |\phi_1(t_0)\rangle + a_2 |\phi_2(t_0)\rangle \quad (2.3)$$

$$\begin{aligned}
|\psi(t)\rangle &= U(t, t_0)|\psi(t_0)\rangle \\
&= U(t, t_0)a_1|\varphi_1(t_0)\rangle + U(t, t_0)a_2|\varphi_2(t_0)\rangle \\
&= a_1(t)|\varphi_1\rangle + a_2(t)|\varphi_2\rangle
\end{aligned} \tag{2.4}$$

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

$$\sum_n |a_n(t)|^2 = \sum_n |a_n(t_0)|^2 \tag{2.5}$$

This dictates that the differential equation of motion is linear in time.

Properties of U

We now make some important and useful observations regarding the properties of U .

- 1) **Unitary.** Note that for eq. (2.5) to hold and for probability density to be conserved, U must be unitary

$$P = \langle \psi(t) | \psi(t) \rangle = \langle \psi(t_0) | U^\dagger U | \psi(t_0) \rangle \tag{2.6}$$

which holds if $U^\dagger = U^{-1}$.

- 2) **Time continuity:** The state is unchanged when the initial and final time-points are the same

$$U(t, t) = 1. \tag{2.7}$$

- 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 ($t_0 \rightarrow t_1 \rightarrow t_2$). Therefore, we can write

$$U(t_2, t_0) = U(t_2, t_1)U(t_1, t_0) \tag{2.8}$$

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

$$\begin{aligned}
|\psi(t_2)\rangle &= U(t_2, t_1)U(t_1, t_0)|\psi(t_0)\rangle \\
&= U(t_2, t_1)|\psi(t_1)\rangle
\end{aligned} \tag{2.9}$$

Equation (2.8) is already very suggestive of an exponential form for U . Furthermore, since time is continuous and the operator is linear it also suggests that the time propagator is only a dependent on a time interval

$$U(t_1, t_0) = U(t_1 - t_0) \tag{2.10}$$

- 4) **Time-reversal.** The inverse of the time-propagator is the time reversal operator. From eq. (2.8):

$$U(t, t_0)U(t_0, t) = 1 \quad (2.11)$$

$$\therefore U^{-1}(t, t_0) = U(t_0, t). \quad (2.12)$$

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 : $U(t + \delta t, t)$. Since

$$\lim_{\delta t \rightarrow 0} U(t + \delta t, t) = 1 \quad (2.13)$$

We expect that for small enough δt , U will change linearly with δt . This is based on analogy to thinking of deterministic motion in classical systems. Setting t_0 to 0, so that $U(t, t_0) = U(t)$, we can write

$$U(t + \delta t) = U(t) - i\hat{\Omega}(t)\delta t \quad (2.14)$$

$\hat{\Omega}$ is a time-dependent Hermitian operator, which is required for U to be unitary. We can now write a differential equation for the time-development of $U(t, t_0)$, the equation of motion for U :

$$\frac{dU(t)}{dt} = \lim_{\delta t \rightarrow 0} \frac{U(t + \delta t) - U(t)}{\delta t} \quad (2.15)$$

So from (2.14) we have:

$$\frac{\partial U(t, t_0)}{\partial t} = -i\hat{\Omega}U(t, t_0) \quad (2.16)$$

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 quantum mechanics fundamentally associates frequency and energy as $E = \hbar\omega$, and since the Hamiltonian is the operator corresponding to the energy, and responsible for time evolution in Hamiltonian mechanics, we write

$$\hat{\Omega} = \frac{\hat{H}}{\hbar} \quad (2.17)$$

With that substitution we have an equation of motion for U :

$$i\hbar \frac{\partial}{\partial t} U(t, t_0) = \hat{H}U(t, t_0) \quad (2.18)$$

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

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = \hat{H} |\psi\rangle \quad (2.19)$$

If you use the Hamiltonian for a free particle $-(\hbar^2/2m)(\partial^2/\partial x^2)$, this looks like a classical wave equation, except that it is linear in time. Rather, this looks like a diffusion equation with imaginary diffusion constant. 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:

$$\langle \psi(t) | = \langle \psi(t_0) | U^\dagger(t, t_0) \quad (2.20)$$

we get

$$-i\hbar \frac{\partial}{\partial t} U^\dagger(t, t_0) = U^\dagger(t, t_0) \hat{H}. \quad (2.21)$$

Evaluating the time-evolution operator

At first glance it may seem straightforward to integrate eq. (2.18). If H is a function of time, then the integration of $i\hbar dU/U = H dt$ gives

$$U(t, t_0) = \exp\left[\frac{-i}{\hbar} \int_{t_0}^t H(t') dt'\right] \quad (2.22)$$

Following our earlier definition of the time-propagator, this exponential would be cast as a series expansion

$$U(t, t_0) \stackrel{?}{=} 1 - \frac{i}{\hbar} \int_{t_0}^t H(t') dt' + \frac{1}{2!} \left(\frac{-i}{\hbar}\right)^2 \int_{t_0}^t \int_{t_0}^t dt' dt'' H(t') H(t'') + \dots \quad (2.23)$$

This approach is dangerous, since we are not properly treating H as an operator. Looking at the second term in eq. (2.23), we see that this expression integrates over both possible time-orderings of the two Hamiltonian operations, which would only be proper if the Hamiltonians at different times commute: $[H(t'), H(t'')] = 0$.

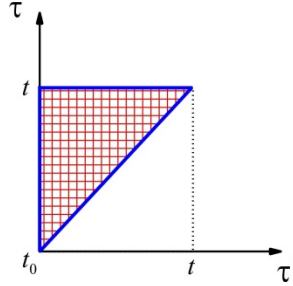
Now, let's proceed a bit more carefully assuming that the Hamiltonians at different times do not commute. Integrating equation (2.18) directly from t_0 to t gives

$$U(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t d\tau H(\tau) U(\tau, t_0) \quad (2.24)$$

This is the solution; however, it is not very practical since $U(t, t_0)$ is a function of itself. But we can make an iterative expansion by repetitive substitution of U into itself. The first step in this process is

$$\begin{aligned}
U(t, t_0) &= 1 - \frac{i}{\hbar} \int_{t_0}^t d\tau H(\tau) \left[1 - \frac{i}{\hbar} \int_{t_0}^{\tau} d\tau' H(\tau') U(\tau', t_0) \right] \\
&= 1 + \left(\frac{-i}{\hbar} \right) \int_{t_0}^t d\tau H(\tau) + \left(\frac{-i}{\hbar} \right)^2 \int_{t_0}^t d\tau \int_{t_0}^{\tau} d\tau' H(\tau) H(\tau') U(\tau', t_0)
\end{aligned}
\tag{2.25}$$

Note in the last term of this equation, that the integration limits enforce a time-ordering; that is, the first integration variable τ' must precede the second τ . Pictorially, the area of integration is

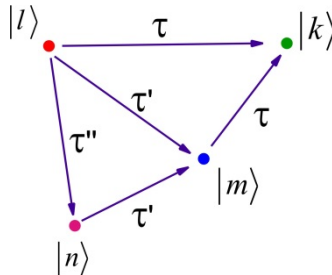


The next substitution step gives

$$\begin{aligned}
U(t, t_0) &= 1 + \left(\frac{-i}{\hbar} \right) \int_{t_0}^t d\tau H(\tau) \\
&\quad + \left(\frac{-i}{\hbar} \right)^2 \int_{t_0}^t d\tau \int_{t_0}^{\tau} d\tau' H(\tau) H(\tau') \\
&\quad + \left(\frac{-i}{\hbar} \right)^3 \int_{t_0}^t d\tau \int_{t_0}^{\tau} d\tau' \int_{t_0}^{\tau'} d\tau'' H(\tau) H(\tau') H(\tau'') U(\tau'', t_0)
\end{aligned}
\tag{2.26}$$

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 : $t_0 \leq \tau'' \leq \tau' \leq \tau \leq t$.

What does this expression represent? Imagine you are starting in state $|\psi_0\rangle = |\ell\rangle$ and you want to describe how one evolves toward a target state $|\psi\rangle = |k\rangle$. The possible paths by which one can shift amplitude and evolve the phase, pictured in terms of these time variables are:



The first term in eq. (2.26) represents all actions of the Hamiltonian which act to directly couple $|\ell\rangle$ and $|k\rangle$. The second term described possible transitions from $|\ell\rangle$ to $|k\rangle$ via an intermediate state $|m\rangle$. The expression for U describes all possible paths between initial and final state. Each

of these paths interferes 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

$$\begin{aligned} U(t, t_0) &\equiv \exp_+ \left[\frac{-i}{\hbar} \int_{t_0}^t d\tau H(\tau) \right] \\ &\equiv \hat{T} \exp \left[\frac{-i}{\hbar} \int_{t_0}^t d\tau H(\tau) \right] \\ &= 1 + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar} \right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \dots \int_{t_0}^{\tau_1} d\tau_1 H(\tau_n) H(\tau_{n-1}) \dots H(\tau_1) \end{aligned} \quad (2.27)$$

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

$$\begin{aligned} t_0 &\rightarrow \tau_1 \rightarrow \tau_2 \rightarrow \tau_3 \dots \tau_n \rightarrow t \\ t_0 &\rightarrow \dots \tau'' \rightarrow \tau' \rightarrow \tau \end{aligned} \quad (2.28)$$

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:

$$1 + \sum_{n=1}^{\infty} \frac{1}{n!} \left(\frac{-i}{\hbar} \right)^n \int_{t_0}^t d\tau_n \dots \int_{t_0}^{\tau_1} d\tau_1 H(\tau_n) H(\tau_{n-1}) \dots H(\tau_1) \quad (2.29)$$

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.) (As commented above these points need some more clarification.)

We are also interested in the Hermitian conjugate of $U(t, t_0)$, which has the equation of motion in eq. (2.21). If we repeat the method above, remembering that $U^\dagger(t, t_0)$ acts to the left, then we obtain

$$U^\dagger(t, t_0) = 1 + \frac{i}{\hbar} \int_{t_0}^t d\tau U^\dagger(t, \tau) H(\tau). \quad (2.30)$$

Performing iterative substitution leads to a negative-time-ordered exponential:

$$\begin{aligned} U^\dagger(t, t_0) &= \exp_- \left[\frac{i}{\hbar} \int_{t_0}^t d\tau H(\tau) \right] \\ &= 1 + \sum_{n=1}^{\infty} \left(\frac{i}{\hbar} \right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \dots \int_{t_0}^{\tau_2} d\tau_1 H(\tau_1) H(\tau_2) \dots H(\tau_n) \end{aligned} \quad (2.31)$$

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

Readings

1. Cohen-Tannoudji, C.; Diu, B.; Lalöe, F., *Quantum Mechanics*. Wiley-Interscience: Paris, 1977; p. 1340.
2. Merzbacher, E., *Quantum Mechanics*. 3rd ed.; Wiley: New York, 1998; Ch. 14.
3. Mukamel, S., *Principles of Nonlinear Optical Spectroscopy*. Oxford University Press: New York, 1995; Ch. 2.
4. Sakurai, J. J., *Modern Quantum Mechanics, Revised Edition*. Addison-Wesley: Reading, MA, 1994; Ch. 2.

2.2. Integrating the TDSE Directly

Okay, how do we evaluate the time-propagator and obtain a time-dependent trajectory for a quantum system? Expressions such as eq. (2.27) are daunting, and there are no simple ways in which to handle this. One cannot truncate the exponential because usually this is not a rapidly converging series. Also, the solutions oscillate rapidly as a result of the phase acquired at the energy of the states involved, which leads to a formidable integration problem. Rapid oscillations require small time steps, when in fact the time scales. For instance in a molecular dynamics problem, the highest frequency oscillations may be as a result of electronically excited states with periods of less than a femtosecond, and the nuclear dynamics that you hope to describe may occur on many picosecond time scales. Rather than general recipes, there exist an arsenal of different strategies that are suited to particular types of problems. The choice of how to proceed is generally dictated by the details of your problem, and is often an art-form. Considerable effort needs to be made to formulate the problem, particularly choosing an appropriate basis set for your problem. Here it is our goal to gain some insight into the types of strategies available, working mainly with the principles, rather than the specifics of how it's implemented.

Let's begin by discussing the most general approach. With adequate computational resources, we can choose the brute force approach of numerical integration. We start by choosing a basis set and defining the initial state ψ_0 . Then, we can numerically evaluate the time-dependence of the wavefunction over a time period t by discretizing time into n small steps of width $\delta t = t/n$ over which the change of the system is small. A variety of strategies can be pursued in practice.

One possibility is to expand your wavefunction in the basis set of your choice

$$|\psi(t)\rangle = \sum_n c_n(t) |\varphi_n\rangle \quad (2.32)$$

and solve for the time-dependence of the expansion coefficients. Substituting into the right side of the TDSE,

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = \hat{H} |\psi\rangle \quad (2.33)$$

and then acting from the left by $\langle k|$ on both sides leads to an equation that describes their time-dependence:

$$i\hbar \frac{\partial c_k(t)}{\partial t} = \sum_n H_{kn}(t) c_n(t) \quad (2.34)$$

or in matrix form $i\hbar \dot{\mathbf{c}} = \mathbf{H}\mathbf{c}$. This represents a set of coupled first-order differential equations in which amplitude flows between different basis states at rates determined by the matrix elements

of the time-dependent Hamiltonian. Such equations are straightforward to integrate numerically. We recognize that we can integrate on a grid if the time step forward (δt) is small enough that the Hamiltonian is essentially constant. Then eq. (2.34) becomes

$$i\hbar \delta c_k(t) = \sum_n H_{kn}(t) c_n(t) \delta t \quad (2.35)$$

and the system is propagated as

$$c_k(t + \delta t) = c_k(t) + \delta c_k(t) \quad (2.36)$$

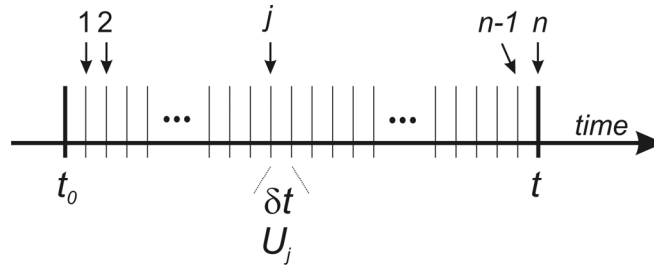
The downside of such a calculation is the unusually small time-steps and significant computational cost required.

Similarly, we can use a grid with short time steps to simplify our time-propagator as

$$\hat{U}(t + \delta t, t) = \exp\left[-\frac{i}{\hbar} \int_t^{t+\delta t} dt' \hat{H}(t')\right] \approx \exp\left[-\frac{i}{\hbar} \delta t \hat{H}(t)\right] \quad (2.37)$$

Therefore the time propagator can be written as a product of n propagators over these small intervals.

$$\begin{aligned} \hat{U}(t) &= \lim_{\delta t \rightarrow 0} [\hat{U}_n \hat{U}_{n-1} \cdots \hat{U}_2 \hat{U}_1] \\ &= \lim_{n \rightarrow \infty} \prod_{j=0}^{n-1} \hat{U}_j \end{aligned} \quad (2.38)$$



Here the time-propagation over the j^{th} small time step is

$$\begin{aligned} \hat{U}_j &= \exp\left[-\frac{i}{\hbar} \delta t \hat{H}_j\right] \\ \hat{H}_j &= \hat{H}(j \delta t) \end{aligned} \quad (2.39)$$

Note that the expressions in (2.38) are operators time ordered from right to left, which we denote with the “+” subscript. Although (2.38) is exact in the limit $\delta t \rightarrow 0$ (or $n \rightarrow \infty$), we can choose a finite number such that $H(t)$ does not change much over the time δt . In this limit the time propagator does not change much and can be approximated as an expansion

$$\hat{U}_j \approx 1 - \frac{i}{\hbar} \delta t \hat{H}_j \quad (2.40)$$

In a general sense this approach is not very practical. The first reason is that the time step is determined by $\delta t \ll \hbar/|H|$ which is typically very small in comparison to the dynamics of interest.

The second complication arises when the potential and kinetic energy operators in the Hamiltonian don't commute. Taking the Hamiltonian to be $\hat{H} = \hat{T} + \hat{V}$,

$$\begin{aligned} e^{-i\hat{H}(t)\delta t/\hbar} &= e^{-i(\hat{T}(t)+\hat{V}(t))\delta t/\hbar} \\ &\approx e^{-i\hat{T}(t)\delta t/\hbar} e^{-i\hat{V}(t)\delta t/\hbar} \end{aligned} \quad (2.41)$$

The second line makes the Split Operator approximation, what states that the time propagator over a short enough period can be approximated as a product of independent propagators evolving the system over the kinetic and potential energy. The validity of this approximation depends on how well these operators commute and the time step, with the error scaling like $\frac{1}{2}[\hat{T}(t), \hat{V}(t)](\delta t / \hbar)^2$, meaning that we should use a time step, such that $\delta t < \{2\hbar^2 / [\hat{T}(t), \hat{V}(t)]\}^{1/2}$.¹ This approximation can be improved by symmetrizing the split operator as

$$e^{-i\hat{H}(t)\delta t/\hbar} \approx e^{-i\hat{V}(t)\frac{\delta t}{2}/\hbar} e^{-i\hat{T}(t)\delta t/\hbar} e^{-i\hat{V}(t)\frac{\delta t}{2}/\hbar} \quad (2.42)$$

Here the error scales as $\frac{1}{12}(\delta t / \hbar)^3 \{[\hat{T}, [\hat{T}, \hat{V}]] + \frac{1}{2}[\hat{V}, [\hat{V}, \hat{T}]]\}$. There is no significant increase in computational effort since half of the operations can be combined as

$$e^{-\frac{i\hat{V}(j+1)\delta t}{\hbar} \frac{1}{2}} e^{-\frac{i\hat{V}(j)\delta t}{\hbar} \frac{1}{2}} \approx e^{-i\hat{V}_j\delta t/\hbar} \quad (2.43)$$

to give

$$U(t) \approx e^{-i\hat{V}\frac{n\delta t}{2}/\hbar} \left[\prod_{j=1}^n e^{-i\hat{V}_j\delta t/\hbar} e^{-i\hat{T}_j\delta t/\hbar} \right] e^{-i\hat{V}\frac{\delta t}{2}/\hbar} \quad (2.44)$$

Readings

1. Tannor, D. J., *Introduction to Quantum Mechanics: A Time-Dependent Perspective*. University Science Books: Sausalito, CA, 2007.

2.3. Transitions Induced by a Time-Dependent Potential

For many time-dependent problems, most notably in spectroscopy, we can often partition the problem so that the time-dependent Hamiltonian contains a time-independent part H_0 that we can describe exactly, and a time-dependent potential $V(t)$:

$$H = H_0 + V(t) \quad (2.45)$$

The remaining degrees of freedom are discarded, and then only enter in the sense that they give rise to the interaction potential with H_0 . This is effective if you have reason to believe that the external Hamiltonian can be treated classically, or if the influence of H_0 on the other degrees of freedom is negligible. From (2.45), 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 .

To begin, we know the complete set of eigenstates and eigenvalues for the system Hamiltonian

$$H_0 |n\rangle = E_n |n\rangle \quad (2.46)$$

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

$$|\psi(t)\rangle = \sum_n c_n(t) |n\rangle \quad (2.47)$$

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

$$c_k(t) = \langle k | \psi(t) \rangle \quad (2.48)$$

Starting with

$$\frac{\partial |\psi\rangle}{\partial t} = \frac{-i}{\hbar} H |\psi\rangle \quad (2.49)$$

$$\frac{\partial c_k(t)}{\partial t} = -\frac{i}{\hbar} \langle k | H | \psi(t) \rangle \quad (2.50)$$

and from (2.50)

$$= -\frac{i}{\hbar} \sum_n \langle k | H | n \rangle c_n(t) \quad (2.51)$$

Already we see that the time evolution amounts to solving a set of coupled linear ordinary differential equations. These are rate equations with complex rate constants, which describe the feeding of one state into another. Substituting eq. (2.45) we have:

$$\begin{aligned} \frac{\partial c_k(t)}{\partial t} &= -\frac{i}{\hbar} \sum_n \langle k | (H_0 + V(t)) | n \rangle c_n(t) \\ &= -\frac{i}{\hbar} \sum_n [E_n \delta_{kn} + V_{kn}(t)] c_n(t) \end{aligned} \quad (2.52)$$

or,

$$\frac{\partial c_k(t)}{\partial t} + \frac{i}{\hbar} E_k c_k(t) = -\frac{i}{\hbar} \sum_n V_{kn}(t) c_n(t). \quad (2.53)$$

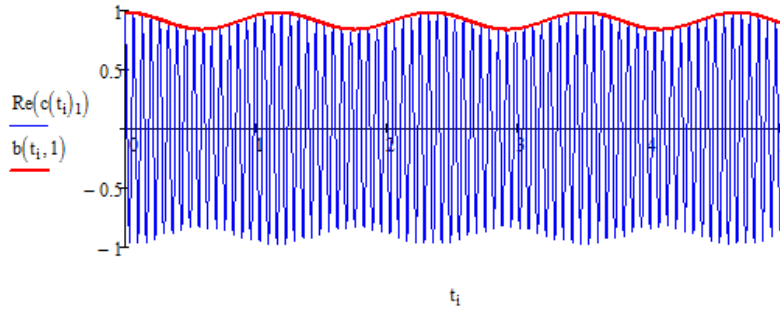
Next, we define and substitute

$$c_m(t) = e^{-iE_m t/\hbar} b_m(t) \quad (2.54)$$

which implies a definition for the wavefunction as

$$|\psi(t)\rangle = \sum_n b_n(t) e^{-iE_n t/\hbar} |n\rangle \quad (2.55)$$

This defines a slightly different complex amplitude, that allows us to simplify things 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, which typically oscillates much faster than the changes to the amplitude of b or c .



We will come back to this strategy which we discuss the interaction picture.

Now eq. (2.53) becomes

$$e^{-iE_k t/\hbar} \frac{\partial b_k}{\partial t} = -\frac{i}{\hbar} \sum_n V_{kn}(t) e^{-iE_n t/\hbar} b_n(t) \quad (2.56)$$

or

$$i\hbar \frac{\partial b_k}{\partial t} = \sum_n V_{kn}(t) e^{-i\omega_{nk} t} b_n(t) \quad (2.57)$$

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 cannot be solved analytically, but it is often straightforward to integrate numerically.

When can we use the approach described here? Consider partitioning the full Hamiltonian into two components, one that we want to study H_0 and the remaining degrees of freedom H_1 . For each part, we have knowledge of the complete eigenstates and eigenvalues of the Hamiltonian: $H_i |\psi_{i,n}\rangle = E_{i,n} |\psi_{i,n}\rangle$. These subsystems will interact with one another through H_{int} . If we are careful to partition this in such a way that H_{int} is small compared H_0 and H_1 , then it

should be possible to properly describe the state of the full system as product states in the sub-systems: $|\psi\rangle = |\psi_0\psi_1\rangle$. Further, we can write a time-dependent Schrödinger equation for the motion of each subsystem as:

$$i\hbar \frac{\partial |\psi_1\rangle}{\partial t} = H_1 |\psi_1\rangle \quad (2.58)$$

Within these assumptions, we can write the complete time-dependent Schrödinger equation in terms of the two sub-states:

$$i\hbar |\psi_0\rangle \frac{\partial |\psi_1\rangle}{\partial t} + i\hbar |\psi_1\rangle \frac{\partial |\psi_0\rangle}{\partial t} = |\psi_0\rangle H_1 |\psi_1\rangle + |\psi_1\rangle H_0 |\psi_0\rangle + H_{\text{int}} |\psi_0\rangle |\psi_1\rangle \quad (2.59)$$

Then left operating by $\langle\psi_1|$ and making use of eq. (2.58), we can write

$$i\hbar \frac{\partial |\psi_0\rangle}{\partial t} = [H_0 + \langle\psi_1| H_{\text{int}} |\psi_1\rangle] |\psi_0\rangle \quad (2.60)$$

This is equivalent to the TDSE for a Hamiltonian of form (2.45) where the external interaction $V(t) = \langle\psi_1| H_{\text{int}}(t) |\psi_1\rangle$ comes from integrating the 1-2 interaction over the sub-space of $|\psi_1\rangle$. So this represents a time-dependent mean field method.

Readings

1. Cohen-Tannoudji, C.; Diu, B.; Lalöe, F., *Quantum Mechanics*. Wiley-Interscience: Paris, 1977; p. 308.
2. Merzbacher, E., *Quantum Mechanics*. 3rd ed.; Wiley: New York, 1998; Ch. 14.
3. Nitzan, A., *Chemical Dynamics in Condensed Phases*. Oxford University Press: New York, 2006; Sec. 2.3.
4. Sakurai, J. J., *Modern Quantum Mechanics, Revised Edition*. Addison-Wesley: Reading, MA, 1994; Ch. 2.

2.4. Resonant Driving of Two-level System

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

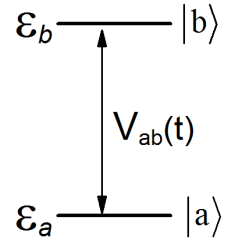
$$V(t) = V \cos \omega t \quad (2.61)$$

$$V_{k\ell}(t) = V_{k\ell} \cos \omega t \quad (2.62)$$

Note, this is the form you would expect for an electromagnetic field interacting with charged particles, i.e. dipole transitions. In a simple sense, the electric field is $\vec{E}(t) = \vec{E}_0 \cos \omega t$ and the interaction potential can be written as $V = -\vec{E} \cdot \vec{\mu}$, where $\vec{\mu}$ represents the dipole operator. We will look at the form of this interaction a bit more carefully later.

We now couple two states $|a\rangle$ and $|b\rangle$ with the oscillating field. Here the energy of the states is ordered so that $\epsilon_b > \epsilon_a$. Let's ask if the system starts in $|a\rangle$ what is the probability of finding it in $|b\rangle$ at time t ?

The system of differential equations that describe this problem is:



$$\begin{aligned} i\hbar \frac{\partial}{\partial t} b_k(t) &= \sum_{n=a,b} b_n(t) V_{kn}(t) e^{-i\omega_{nk}t} \\ &= \sum_{n=a,b} b_n(t) V_{kn} e^{-i\omega_{nk}t} \cdot \frac{1}{2} (e^{-i\omega t} + e^{i\omega t}) \end{aligned} \quad (2.63)$$

Where I wrote $\cos \omega t$ in its complex form. Writing this explicitly

$$i\hbar \dot{b}_b = \frac{1}{2} b_a V_{ba} \left[e^{i(\omega_{ba}-\omega)t} + e^{i(\omega_{ba}+\omega)t} \right] + \frac{1}{2} b_b V_{bb} \left[e^{i\omega t} + e^{-i\omega t} \right] \quad (2.64)$$

$$\begin{aligned} i\hbar \dot{b}_a &= \frac{1}{2} b_a V_{aa} \left[e^{i\omega t} + e^{-i\omega t} \right] + \frac{1}{2} b_b V_{ab} \left[\underbrace{e^{i(\omega_{ab}-\omega)t} + e^{i(\omega_{ab}+\omega)t}}_{\text{or}} \right] \\ &\quad \left[e^{-i(\omega_{ba}+\omega)t} + e^{-i(\omega_{ba}-\omega)t} \right] \end{aligned} \quad (2.65)$$

Here the expressions have been written in terms of the frequency ω_{ba} . Two of these terms are dropped, since (for our case) the diagonal matrix elements $V_{ii} = 0$. We also make the *secular approximation* (or *rotating wave approximation*) in which the nonresonant terms are dropped. When $\omega_{ba} \approx \omega$, terms like $e^{\pm i\omega t}$ or $e^{i(\omega_{ba}+\omega)t}$ oscillate very rapidly (relative to $|V_{ba}|^{-1}$) and so do not contribute much to change of c_n . (Remember, we take the frequencies ω_{ba} and ω to be positive). So now we have:

$$\dot{b}_b = \frac{-i}{2\hbar} b_a V_{ba} e^{i(\omega_{ba}-\omega)t} \quad (2.66)$$

$$\dot{b}_a = \frac{-i}{2\hbar} b_b V_{ab} e^{-i(\omega_{ba}-\omega)t} \quad (2.67)$$

Note that the coefficients are oscillating at the same frequency but phase shifted to one another. Now if we differentiate eq. (2.66):

$$\ddot{b}_b = \frac{-i}{2\hbar} \left[\dot{b}_a V_{ba} e^{i(\omega_{ba}-\omega)t} + i(\omega_{ba}-\omega) b_a V_{ba} e^{i(\omega_{ba}-\omega)t} \right] \quad (2.68)$$

Rewrite eq. (2.66):

$$b_a = \frac{2i\hbar}{V_{ba}} \dot{b}_b e^{-i(\omega_{ba}-\omega)t} \quad (2.69)$$

and substitute (2.69) and (2.67) into (2.68), we get linear second order equation for b_b .

$$\ddot{b}_b - i(\omega_{ba}-\omega)\dot{b}_b + \frac{|V_{ba}|^2}{4\hbar^2} b_b = 0 \quad (2.70)$$

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

$$a\ddot{x} + b\dot{x} + cx = 0 \quad (2.71)$$

$$x = e^{-(b/2a)t} (A \cos \mu t + B \sin \mu t) \quad (2.72)$$

$$\mu = \frac{1}{2a} \sqrt{4ac - b^2} \quad (2.72)$$

With a little more manipulation, and remembering the initial conditions $b_k(0) = 0$ and $b_l(0) = 1$, we find

$$P_b(t) = |b_b(t)|^2 = \frac{|V_{ba}|^2}{|V_{ba}|^2 + \hbar^2(\omega_{ba}-\omega)^2} \sin^2 \Omega_R t \quad (2.73)$$

Where the Rabi Frequency

$$\Omega_R = \frac{1}{2\hbar} \sqrt{|V_{ba}|^2 + \hbar^2(\omega_{ba}-\omega)^2} \quad (2.74)$$

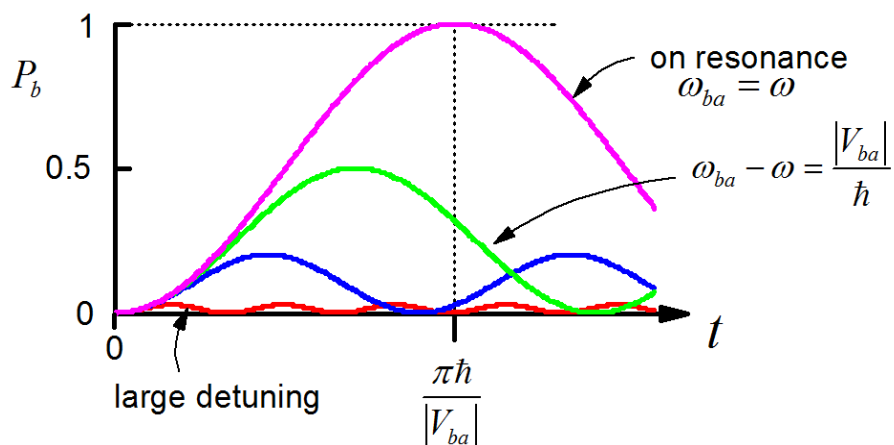
Also,

$$P_a = 1 - P_b \quad (2.75)$$

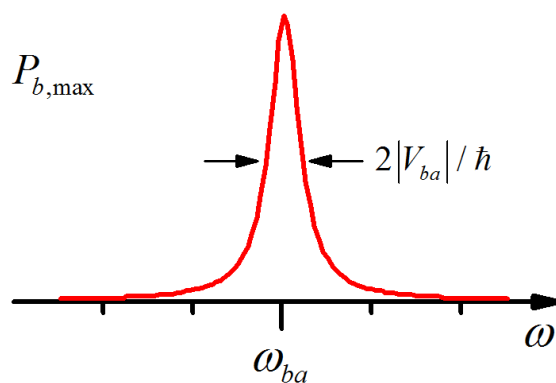
The amplitude oscillates back and forth between the two states at a frequency dictated by the coupling between them. [Note a result we will return to later: electric fields couple quantum states, creating coherences!]

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 a and b states drops off with detuning. Here plotting the maximum value of P_b as a function of frequency:



2.5. Schrödinger and Heisenberg Representations

The mathematical formulation of quantum dynamics that has been presented is not unique. So far, we have described the dynamics by propagating the wavefunction, which encodes probability densities. Ultimately, since we cannot measure a wavefunction, we are interested in observables, which are probability amplitudes associated with Hermitian operators, with time-dependence that can be interpreted differently. Consider the expectation value:

$$\begin{aligned}\langle \hat{A}(t) \rangle &= \langle \psi(t) | \hat{A} | \psi(t) \rangle = \langle \psi(0) | U^\dagger \hat{A} U | \psi(0) \rangle \\ &= (\langle \psi(0) | U^\dagger) \hat{A} (U | \psi(0) \rangle) \\ &= \langle \psi(0) | (U^\dagger \hat{A} U) | \psi(0) \rangle\end{aligned}\quad (2.76)$$

The last two expressions are written to emphasize alternate “pictures” of the dynamics. The first, known as the Schrödinger picture, refers to everything we have done so far. Here we propagate the wavefunction or eigenvectors in time as $U|\psi\rangle$. Operators are unchanged because they carry no time-dependence. Alternatively, we can work in the Heisenberg picture. This uses the unitary property of U to time-propagate the operators as $\hat{A}(t) = U^\dagger \hat{A} U$, but the wavefunction is now stationary. The Heisenberg picture has an appealing physical picture behind it, because particles move. That is, there is a time-dependence to position and momentum.

Schrödinger Picture

In the Schrödinger picture, the time-development of $|\psi\rangle$ is governed by the TDSE or equivalently, the time propagator:

$$i\hbar \frac{\partial}{\partial t} |\psi\rangle = H |\psi\rangle \quad \text{and} \quad |\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle \quad (2.77)$$

In the Schrödinger picture, operators are typically independent of time, $\partial A / \partial t = 0$. What about observables? For expectation values of operators $\langle A(t) \rangle = \langle \psi | A | \psi \rangle$:

$$\begin{aligned}i\hbar \frac{\partial}{\partial t} \langle \hat{A}(t) \rangle &= i\hbar \left[\left\langle \psi \left| \hat{A} \frac{\partial \psi}{\partial t} \right\rangle + \left\langle \frac{\partial \psi}{\partial t} \left| \hat{A} \right| \psi \right\rangle + \left\langle \psi \left| \frac{\partial \hat{A}}{\partial t} \right| \psi \right\rangle \right] \\ &= \langle \psi | \hat{A} H | \psi \rangle - \langle \psi | H \hat{A} | \psi \rangle \\ &= \langle [\hat{A}, H] \rangle\end{aligned}\quad (2.78)$$

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. (2.76), we can distinguish the Schrödinger picture from Heisenberg operators:

$$\hat{A}(t) = \langle \psi(t) | \hat{A} | \psi(t) \rangle_S = \langle \psi(t_0) | U^\dagger \hat{A} U | \psi(t_0) \rangle_S = \langle \psi | \hat{A}(t) | \psi \rangle_H \quad (2.79)$$

where the operator is defined as

$$\begin{aligned} \hat{A}_H(t) &= U^\dagger(t, t_0) \hat{A}_S U(t, t_0) \\ \hat{A}_H(t_0) &= \hat{A}_S \end{aligned} \quad (2.80)$$

Note, the pictures have the same wavefunction at the reference point t_0 . Since the wavefunction should be time-independent, $\partial |\psi_H\rangle / \partial t = 0$, we can relate the Schrödinger and Heisenberg wavefunctions as

$$|\psi_S(t)\rangle = U(t, t_0) |\psi_H\rangle \quad (2.81)$$

$$\text{So,} \quad |\psi_H\rangle = U^\dagger(t, t_0) |\psi_S(t)\rangle = |\psi_S(t_0)\rangle \quad (2.82)$$

As expected for a unitary transformation, in either picture the eigenvalues are preserved:

$$\begin{aligned} \hat{A} |\varphi_i\rangle_S &= a_i |\varphi_i\rangle_S \\ U^\dagger \hat{A} U U^\dagger |\varphi_i\rangle_S &= a_i U^\dagger |\varphi_i\rangle_S \\ \hat{A}_H |\varphi_i\rangle_H &= a_i |\varphi_i\rangle_H \end{aligned} \quad (2.83)$$

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

$$\begin{aligned} \frac{\partial \hat{A}_H}{\partial t} &= \frac{\partial}{\partial t} (U^\dagger \hat{A}_S U) = \frac{\partial U^\dagger}{\partial t} \hat{A}_S U + U^\dagger \hat{A}_S \frac{\partial U}{\partial t} + U^\dagger \frac{\partial \hat{A}_S}{\partial t} U \\ &= \frac{i}{\hbar} U^\dagger H \hat{A}_S U - \frac{i}{\hbar} U^\dagger \hat{A}_S H U + \left(\frac{\partial \hat{A}_S}{\partial t} \right)_H \\ &= \frac{i}{\hbar} H_H \hat{A}_H - \frac{i}{\hbar} \hat{A}_H H_H \\ &= -\frac{i}{\hbar} [\hat{A}, H]_H \end{aligned} \quad (2.84)$$

$$\text{The result} \quad i\hbar \frac{\partial}{\partial t} \hat{A}_H = [\hat{A}, H]_H \quad (2.85)$$

is known as the Heisenberg equation of motion. Here I have written the odd looking $H_H = U^\dagger H U$. This is mainly to remind one about the time-dependence of H . 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.

Classical equivalence for particle in a potential

The Heisenberg equation is commonly applied to a particle in an arbitrary potential. Consider a particle with an arbitrary one-dimensional potential

$$H = \frac{p^2}{2m} + V(x) \quad (2.86)$$

For this Hamiltonian, the Heisenberg equation gives the time-dependence of the momentum and position as

$$\dot{p} = -\frac{\partial V}{\partial x} \quad (2.87)$$

$$\dot{x} = \frac{p}{m} \quad (2.88)$$

Here, I have made use of

$$[\hat{x}^n, \hat{p}] = i\hbar n\hat{x}^{n-1} \quad (2.89)$$

$$[\hat{x}, \hat{p}^n] = i\hbar n\hat{p}^{n-1} \quad (2.90)$$

Curiously, the factors of \hbar have vanished in equations (2.87) and (2.88), and quantum mechanics does not seem to be present. Instead, these equations indicate that the position and momentum operators follow the same equations of motion as Hamilton's equations for the classical variables. If we integrate eq. (2.88) over a time period t we find that the expectation value for the position of the particle follows the classical motion.

$$\langle x(t) \rangle = \frac{\langle p \rangle t}{m} + \langle x(0) \rangle \quad (2.91)$$

We can also use the time derivative of eq. (2.88) to obtain an equation that mirrors Newton's second law of motion, $F=ma$:

$$m \frac{\partial^2 \langle x \rangle}{\partial t^2} = -\langle \nabla V \rangle \quad (2.92)$$

These observations underlie Ehrenfest's Theorem, a statement of the classical correspondence of quantum mechanics, which states that the expectation values for the position and momentum operators will follow the classical equations of motion.

Readings

1. Cohen-Tannoudji, C.; Diu, B.; Lalöe, F., *Quantum Mechanics*. Wiley-Interscience: Paris, 1977; p. 312.
2. Mukamel, S., *Principles of Nonlinear Optical Spectroscopy*. Oxford University Press: New York, 1995.
3. Nitzan, A., *Chemical Dynamics in Condensed Phases*. Oxford University Press: New York, 2006; Ch. 4.

4. Sakurai, J. J., *Modern Quantum Mechanics, Revised Edition*. Addison-Wesley: Reading, MA, 1994; Ch. 2.

2.6. 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

$$H(t) = H_0 + V(t) \quad (2.93)$$

H_0 is a Hamiltonian for the degrees of freedom we are interested in, which we treat exactly, and can be (although for us usually will not 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. If H_0 is not a function of time, then there is a 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

$$\frac{\partial}{\partial t} U_0(t, t_0) = -\frac{i}{\hbar} H_0(t) U_0(t, t_0) \quad (2.94)$$

where,

$$U_0(t, t_0) = \exp_+ \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau H_0(\tau) \right] \quad (2.95)$$

or, for a time-independent H_0 ,

$$U_0(t, t_0) = e^{-iH_0(t-t_0)/\hbar} \quad (2.96)$$

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

$$|\psi_S(t)\rangle \equiv U_0(t, t_0) |\psi_I(t)\rangle \quad (2.97)$$

or

$$|\psi_I\rangle = U_0^\dagger |\psi_S\rangle \quad (2.98)$$

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 induced by V .

Now we need an equation of motion that describes the time evolution of the interaction picture wavefunctions. We begin by substituting eq. (2.97) into the TDSE:

$$i\hbar \frac{\partial}{\partial t} |\psi_S\rangle = H |\psi_S\rangle \quad (2.99)$$

$$\begin{aligned} \frac{\partial}{\partial t} U_0(t, t_0) |\psi_I\rangle &= \frac{-i}{\hbar} H(t) U_0(t, t_0) |\psi_I\rangle \\ \frac{\partial U_0}{\partial t} |\psi_I\rangle + U_0 \frac{\partial |\psi_I\rangle}{\partial t} &= \frac{-i}{\hbar} (H_0 + V(t)) U_0(t, t_0) |\psi_I\rangle \\ \frac{-i}{\hbar} H_0 U_0 |\psi_I\rangle + U_0 \frac{\partial |\psi_I\rangle}{\partial t} &= \frac{-i}{\hbar} (H_0 + V(t)) U_0 |\psi_I\rangle \end{aligned} \quad (2.100)$$

$$\therefore i\hbar \frac{\partial |\psi_I\rangle}{\partial t} = V_I |\psi_I\rangle \quad (2.101)$$

where

$$V_I(t) = U_0^\dagger(t, t_0) V(t) U_0(t, t_0) \quad (2.102)$$

$|\psi_I\rangle$ satisfies the Schrödinger equation with a new Hamiltonian in eq. (2.102): the interaction picture Hamiltonian, $V_I(t)$. We have performed a unitary transformation of $V(t)$ into the frame of reference of H_0 , using U_0 . 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:

$$|\psi_I(t)\rangle = U_I(t, t_0) |\psi_I(t_0)\rangle \quad (2.103)$$

where

$$U_I(t, t_0) = \exp_+ \left[\frac{-i}{\hbar} \int_{t_0}^t d\tau V_I(\tau) \right] \quad (2.104)$$

Now we see that

$$\begin{aligned} |\psi_S(t)\rangle &= U_0(t, t_0) |\psi_I(t)\rangle \\ &= U_0(t, t_0) U_I(t, t_0) |\psi_I(t_0)\rangle \\ &= U_0(t, t_0) U_I(t, t_0) |\psi_S(t_0)\rangle \end{aligned} \quad (2.105)$$

$$\therefore U(t, t_0) = U_0(t, t_0) U_I(t, t_0) \quad (2.106)$$

Also, the time evolution of conjugate wavefunction in the interaction picture can be written

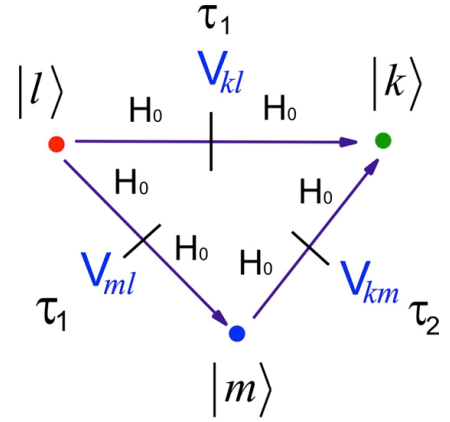
$$U^\dagger(t, t_0) = U_I^\dagger(t, t_0) U_0^\dagger(t, t_0) = \exp_- \left[\frac{i}{\hbar} \int_{t_0}^t d\tau V_I(\tau) \right] \exp_- \left[\frac{i}{\hbar} \int_{t_0}^t d\tau H_0(\tau) \right] \quad (2.107)$$

For the last two expressions, the order of these operators certainly matters.

So what changes about the time-propagation in the interaction representation? Let's start by writing out the time-ordered exponential for U in eq. (2.106) using eq. (2.104):

$$\begin{aligned}
U(t, t_0) &= U_0(t, t_0) + \left(\frac{-i}{\hbar}\right) \int_{t_0}^t d\tau U_0(t, \tau) V(\tau) U_0(\tau, t_0) + \dots \\
&= U_0(t, t_0) + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \dots \int_{t_0}^{\tau_2} d\tau_1 U_0(t, \tau_n) V(\tau_n) U_0(\tau_n, \tau_{n-1}) \dots \\
&\quad \times U_0(\tau_2, \tau_1) V(\tau_1) U_0(\tau_1, t_0)
\end{aligned} \tag{2.108}$$

Here I 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. (2.102) and collected terms. Now consider how U describes the time-dependence if I initiate the system in an eigenstate of H_0 $|l\rangle$ and observe the amplitude in a target eigenstate $|k\rangle$. 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 first-order term describes direct transitions between l and k induced by V , integrated over the full time period. Before the interaction phase is acquired as $e^{-iE_l(\tau-t_0)/\hbar}$, whereas after the interaction phase is acquired as $e^{-iE_k(t-\tau)/\hbar}$. Higher-order terms in the time-ordered exponential accounts for all possible intermediate pathways.



We now know how the interaction picture wavefunctions evolve in time. What about the operators? First of all, from examining the expectation value of an operator we see

$$\begin{aligned}
\langle \hat{A}(t) \rangle &= \langle \psi(t) | \hat{A} | \psi(t) \rangle \\
&= \langle \psi(t_0) | U^\dagger(t, t_0) \hat{A} U(t, t_0) | \psi(t_0) \rangle \\
&= \langle \psi(t_0) | U_I^\dagger U_0^\dagger \hat{A} U_0 U_I | \psi(t_0) \rangle \\
&= \langle \psi_I(t) | \hat{A}_I | \psi_I(t) \rangle
\end{aligned} \tag{2.109}$$

where
$$A_I \equiv U_0^\dagger A_S U_0. \tag{2.110}$$

So the operators in the interaction picture also evolve in time, but under H_0 . This can be expressed as a Heisenberg equation by differentiating A_I

$$\frac{\partial}{\partial t} \hat{A}_I = \frac{i}{\hbar} [H_0, \hat{A}_I] \tag{2.111}$$

Also, we know
$$\frac{\partial}{\partial t} |\psi_I\rangle = \frac{-i}{\hbar} V_I(t) |\psi_I\rangle \tag{2.112}$$

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 .

$$\begin{aligned} \text{For } H_0 = 0, V(t) = H &\Rightarrow \frac{\partial \hat{A}}{\partial t} = 0; \quad \frac{\partial}{\partial t} |\psi_S\rangle = \frac{-i}{\hbar} H |\psi_S\rangle && \text{Schrödinger} \\ \text{For } H_0 = H, V(t) = 0 &\Rightarrow \frac{\partial \hat{A}}{\partial t} = \frac{i}{\hbar} [H, \hat{A}]; \quad \frac{\partial \psi}{\partial t} = 0 && \text{Heisenberg} \end{aligned} \quad (2.113)$$

The relationship between U_I and b_n

Earlier we described how time-dependent problems with Hamiltonians of the form $H = H_0 + V(t)$ could be solved in terms of the time-evolving amplitudes in the eigenstates of H_0 . We can describe the state of the system as a superposition

$$|\psi(t)\rangle = \sum_n c_n(t) |n\rangle \quad (2.114)$$

where the expansion coefficients $c_k(t)$ are given by

$$\begin{aligned} c_k(t) &= \langle k | \psi(t) \rangle = \langle k | U(t, t_0) | \psi(t_0) \rangle \\ &= \langle k | U_0 U_I | \psi(t_0) \rangle \\ &= e^{-iE_k t / \hbar} \langle k | U_I | \psi(t_0) \rangle \end{aligned} \quad (2.115)$$

Now, comparing equations (2.115) and (2.54) allows us to recognize that our earlier modified expansion coefficients b_n were expansion coefficients for interaction picture wavefunctions

$$b_k(t) = \langle k | \psi_I(t) \rangle = \langle k | U_I | \psi(t_0) \rangle \quad (2.116)$$

Readings

1. Mukamel, S., *Principles of Nonlinear Optical Spectroscopy*. Oxford University Press: New York, 1995.
2. Nitzan, A., *Chemical Dynamics in Condensed Phases*. Oxford University Press: New York, 2006; Ch. 4.

2.7. Time-Dependent Perturbation Theory

Perturbation theory refers to calculating the time-dependence of a system by truncating the expansion of the interaction picture time-evolution operator after a certain term. In practice, truncating the full time-propagator U is not effective, and only works well for times short compared to the inverse of the energy splitting between coupled states of your Hamiltonian. The interaction picture applies to Hamiltonians that can be cast as $H(t) = H_0 + V(t)$ and, allows us to focus on the influence of the coupling. We can then treat the time evolution under H_0 exactly, but truncate the influence of $V(t)$. This works well for weak perturbations. Let's look more closely at this.

We know the eigenstates for H_0 : $H_0|n\rangle = E_n|n\rangle$, and we can calculate the evolution of the wavefunction that results from $V(t)$:

$$|\psi_I(t)\rangle = \sum_n b_n(t)|n\rangle \quad (2.117)$$

For a given state k , we calculate $b_k(t)$ as:

$$b_k = \langle k|U_I(t, t_0)|\psi(t_0)\rangle \quad (2.118)$$

where

$$U_I(t, t_0) = \exp_+ \left[\frac{-i}{\hbar} \int_{t_0}^t V_I(\tau) d\tau \right] \quad (2.119)$$

Now we can truncate the expansion after a few terms. 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 will see, the results we obtain from perturbation theory are widely used for spectroscopy, condensed phase dynamics, and relaxation.

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 $V(t)$: $P_k(t) = |b_k(t)|^2$.

$$\text{Expanding} \quad b_k(t) = \left\langle k \left| \exp_+ \left[-\frac{i}{\hbar} \int_{t_0}^t d\tau V_I(\tau) \right] \right| \ell \right\rangle \quad (2.120)$$

$$\begin{aligned} b_k(t) &= \langle k|\ell\rangle - \frac{i}{\hbar} \int_{t_0}^t d\tau \langle k|V_I(\tau)|\ell\rangle \\ &+ \left(\frac{-i}{\hbar} \right)^2 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 \langle k|V_I(\tau_2)V_I(\tau_1)|\ell\rangle + \dots \end{aligned} \quad (2.121)$$

$$\text{Now, using} \quad \langle k|V_I(t)|\ell\rangle = \langle k|U_0^\dagger V(t)U_0|\ell\rangle = e^{-i\omega_{k\ell}t} V_{k\ell}(t) \quad (2.122)$$

we obtain:

$$b_k(t) = \delta_{k\ell} - \frac{i}{\hbar} \int_{t_0}^t d\tau_1 e^{-i\omega_{\ell k}\tau_1} V_{k\ell}(\tau_1) \quad \text{“first-order”} \quad (2.123)$$

$$+ \sum_m \left(\frac{-i}{\hbar} \right)^2 \int_{t_0}^t d\tau_2 \int_{t_0}^{\tau_2} d\tau_1 e^{-i\omega_{mk}\tau_2} V_{km}(\tau_2) e^{-i\omega_{\ell m}\tau_1} V_{m\ell}(\tau_1) \quad \text{“second order”} \quad (2.124)$$

+ ...

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. (2.123) is the solution to the differential equation that you get for direct coupling between $|\ell\rangle$ and $|k\rangle$:

$$\frac{\partial}{\partial t} b_k = \frac{-i}{\hbar} e^{-i\omega_{\ell k}t} V_{k\ell}(t) b_\ell(0) \quad (2.125)$$

This indicates that the solution does not allow for the feedback between $|\ell\rangle$ and $|k\rangle$ that accounts for changing populations. This is the reason we say that validity dictates $|b_k(t)|^2 - |b_k(0)|^2 \ll 1$. If the initial state of the system $|\psi_0\rangle$ is not an eigenstate of H_0 , we can express it as a superposition of eigenstates, $|\psi_0\rangle = \sum_n b_n(0)|n\rangle$ with

$$b_k(t) = \sum_n b_n(0) \langle k|U_I|n\rangle \quad (2.126)$$

Another observation applies to first-order perturbation theory. 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 related to the Fourier transform of $V_{\ell k}(t)$ evaluated at the energy gap $\omega_{\ell k}$.

$$b_k(t) = -\frac{i}{\hbar} \int_{-\infty}^{+\infty} d\tau e^{-i\omega_{\ell k}\tau} V_{k\ell}(\tau) \quad (2.127)$$

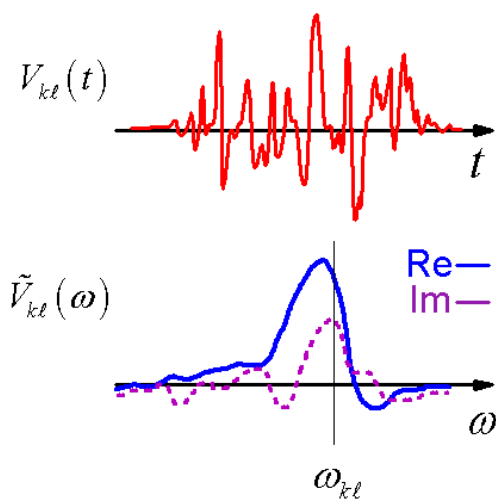
If the Fourier transform pair is defined in the following manner:

$$\tilde{V}(\omega) \equiv \tilde{\mathcal{F}}[V(t)] = \int_{-\infty}^{+\infty} dt V(t) \exp(i\omega t), \quad (2.128)$$

$$V(t) \equiv \tilde{\mathcal{F}}^{-1}[\tilde{V}(\omega)] = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \tilde{V}(\omega) \exp(-i\omega t) \quad (2.129)$$

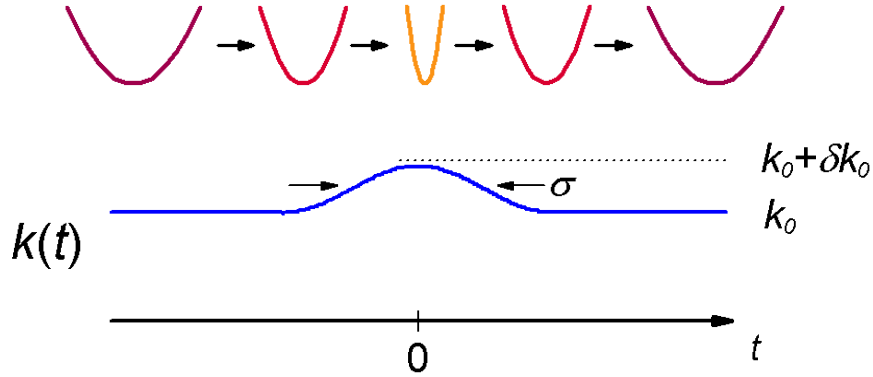
Then we can write the probability of transfer to state k as

$$P_{kl} = \frac{2\pi |\tilde{V}_{kl}(\omega_{kl})|^2}{\hbar^2}. \quad (2.130)$$



Example: First-order Perturbation Theory

Let's consider a simple model for vibrational excitation induced by the compression of harmonic oscillator. We will subject a harmonic oscillator initially in its ground state to a Gaussian compression pulse, which increases its force constant.



First, write the complete time-dependent Hamiltonian:

$$H(t) = T + V(t) = \frac{p^2}{2m} + \frac{1}{2}k(t)x^2 \quad (2.131)$$

Now, partition it according to $H = H_0 + V(t)$ in such a manner that we can write H_0 as a harmonic oscillator Hamiltonian. This involves partitioning the time-dependent force constant into two parts:

$$k(t) = k_0 + \delta k(t) \quad k_0 = m\Omega^2 \quad \delta k(t) = \delta k_0 \exp\left(-\frac{(t-t_0)^2}{2\sigma^2}\right) \quad (2.132)$$

$$H = \underbrace{\frac{p^2}{2m} + \frac{1}{2}k_0x^2}_{H_0} + \underbrace{\frac{1}{2}\delta k_0x^2 \exp\left(-\frac{(t-t_0)^2}{2\sigma^2}\right)}_{V(t)} \quad (2.133)$$

Here δk_0 is the magnitude of the induced change in the force constant, and σ is the time-width of the Gaussian perturbation. So, we know the eigenstates of H_0 : $H_0 |n\rangle = E_n |n\rangle$

$$H_0 = \hbar\Omega \left(a^\dagger a + \frac{1}{2} \right) \quad E_n = \hbar\Omega \left(n + \frac{1}{2} \right) \quad (2.134)$$

Now we ask, if the system is in $|0\rangle$ before applying the perturbation, what is the probability of finding it in state $|n\rangle$ after the perturbation?

For $n \neq 0$:

$$b_n(t) = \frac{-i}{\hbar} \int_{t_0}^t d\tau V_{n0}(\tau) e^{i\omega_{n0}\tau} \quad (2.135)$$

Using $\omega_{n0} = (E_n - E_0)/\hbar = n\Omega$, and recognizing that we can set the limits to $t_0 = -\infty$ and $t = \infty$,

$$b_n(t) = \frac{-i}{2\hbar} \delta k_0 \langle n|x^2|0\rangle \int_{-\infty}^{+\infty} d\tau e^{in\Omega\tau} e^{-\tau^2/2\sigma^2} \quad (2.136)$$

This leads to

$$b_n(t) = \frac{-i}{2\hbar} \delta k_0 \sqrt{2\pi}\sigma \langle n|x^2|0\rangle e^{-n^2\sigma^2\Omega^2/2} \quad (2.137)$$

Here we made use of an important identity for Gaussian integrals:

$$\int_{-\infty}^{+\infty} \exp(ax^2 + bx + c) dx = \sqrt{\frac{-\pi}{a}} \exp\left(c - \frac{1}{4} \frac{b^2}{a}\right) \quad (2.138)$$

$$\int_{-\infty}^{+\infty} \exp(-ax^2 + ibx) dx = \sqrt{\frac{\pi}{a}} \exp\left(-\frac{b^2}{4a}\right) \quad (2.139)$$

What about the matrix element?

$$x^2 = \frac{\hbar}{2m\Omega} (a + a^\dagger)^2 = \frac{\hbar}{2m\Omega} (aa + a^\dagger a + aa^\dagger + a^\dagger a^\dagger) \quad (2.140)$$

From these we see that first-order perturbation theory will not allow transitions to $n=1$, only $n=0$ and $n=2$. Generally this would not be realistic, because you would certainly expect excitation to $n=1$ would dominate over excitation to $n=2$. 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,

$$\langle 2|x^2|0\rangle = \sqrt{2} \frac{\hbar}{2m\Omega} \quad (2.141)$$

So,

$$b_2 = \frac{-i\sqrt{\pi}\delta k_0\sigma}{2m\Omega} e^{-2\sigma^2\Omega^2} \quad (2.142)$$

and we can write the probability of occupying the $n=2$ state as

$$P_2 = |b_2|^2 = \frac{\pi\delta k_0^2\sigma^2}{2m^2\Omega^2} e^{-4\sigma^2\Omega^2} \quad (2.143)$$

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

$$\sigma \ll \frac{1}{\Omega} \quad (2.144)$$

In this regime, the potential is changing faster than the atoms can respond to the perturbation. In practice, when considering a solid-state problem, with frequencies matching those of acoustic phonons and unit cell dimensions, we need perturbations that move faster than the speed of sound, i.e., a shock wave. The opposite limit, $\sigma\Omega \gg 1$, is the adiabatic limit. In this case, the perturbation is so slow that the system always remains entirely in $n=0$, even while it is compressed.

Now, let's consider the validity of this first-order treatment. Perturbation theory does not allow for b_n to change much from its initial value. First we re-write eq. (2.143) as

$$P_2 = \sigma^2 \Omega^2 \frac{\pi}{2} \left(\frac{\delta k_0^2}{k_0^2} \right) e^{-4\sigma^2 \Omega^2} \quad (2.145)$$

Now for changes that don't differ much from the initial value, $P_2 \ll 1$

$$\sigma^2 \Omega^2 \frac{\pi}{2} \left(\frac{\delta k_0^2}{k_0^2} \right) \ll 1 \quad (2.146)$$

Generally, the magnitude of the perturbation δk_0 must be small compared to k_0 .

One step further...

The preceding example was simple, but it tracks the general approach to setting up problems that you treat with time-dependent perturbation theory. The approach relies on writing a Hamiltonian that can be cast into a Hamiltonian that you can treat exactly H_0 , and time-dependent perturbations that shift amplitudes between its eigenstates. For this scheme to work well, we need the magnitude of perturbation to be small, which immediately suggests working with a Taylor series expansion of the potential. For instance, take a one-dimensional potential for a bound particle, $V(x)$, which is dependent on the form of an external variable y . We can expand the potential in x about its minimum $x = 0$ as

$$\begin{aligned} V(x) &= \frac{1}{2!} \left. \frac{\partial^2 V}{\partial x^2} \right|_{x=0} x^2 + \frac{1}{2!} \left. \frac{\partial^2 V}{\partial x \partial y} \right|_{x=0} xy + \frac{1}{3!} \sum_{y,z} \left. \frac{\partial^3 V}{\partial x \partial y \partial z} \right|_{x=0} xyz + \dots \\ &= \frac{1}{2} kx^2 + V^{(2)} xy + \left(V_3^{(3)} x^3 + V_2^{(3)} x^2 y + V_1^{(3)} xy^2 \right) + \dots \end{aligned} \quad (2.147)$$

The first term is the harmonic force constant for x , and the second term is a bi-linear coupling whose magnitude $V^{(2)}$ indicates how much a change in the variable y influences the variable x . The remaining terms are cubic expansion terms. $V_3^{(3)}$ is the cubic anharmonicity of $V(x)$, and the remaining two terms are cubic couplings that describe the dependence of x on y . Introducing a time-dependent potential is equivalent to introducing a time-dependence to the operator y , where the form and strength of the interaction is subsumed into the amplitude V . In the case of the

previous example, our formulation of the problem was equivalent to selecting only the $V_2^{(3)}$ term, so that $\delta k_0/2 = V_2^{(3)}$, and giving the value of y a time-dependence described by the Gaussian waveform.

Readings

1. Cohen-Tannoudji, C.; Diu, B.; Lalöe, F., *Quantum Mechanics*. Wiley-Interscience: Paris, 1977; p. 1285.
2. Nitzan, A., *Chemical Dynamics in Condensed Phases*. Oxford University Press: New York, 2006; Ch. 4.
3. Sakurai, J. J., *Modern Quantum Mechanics, Revised Edition*. Addison-Wesley: Reading, MA, 1994; Ch. 2.

2.8. Fermi's Golden Rule

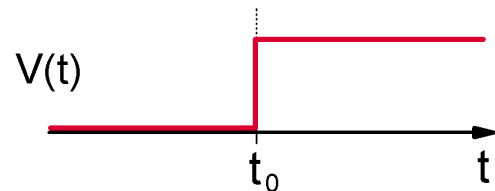
A number of important relationships in quantum mechanics that describe rate processes come from first-order perturbation theory. These expressions begin with two model problems that we want to work through: (1) time evolution after applying a step perturbation, and (2) time evolution after applying a harmonic perturbation. As before, we will ask: if we prepare the system in the state $|\ell\rangle$, what is the probability of observing the system in state $|k\rangle$ following the perturbation?

Constant perturbation (or step perturbation)

The system is prepared such that $|\psi(-\infty)\rangle = |\ell\rangle$. A constant perturbation of amplitude V is applied at t_0 :

$$V(t) = V \Theta(t - t_0) = \begin{cases} 0 & t < t_0 \\ V & t \geq t_0 \end{cases} \quad (2.148)$$

Here $\Theta(t - t_0)$ is the Heaviside step response function, which is 0 for $t < t_0$ and 1 for $t \geq t_0$. Now, turning to first-order perturbation theory, the amplitude in $k \neq \ell$, we have:



$$b_k = -\frac{i}{\hbar} \int_{t_0}^t d\tau e^{i\omega_{k\ell}(\tau - t_0)} V_{k\ell}(\tau) \quad (2.149)$$

Here $V_{k\ell}$ is independent of time. Setting $t_0 = 0$,

$$\begin{aligned} b_k &= -\frac{i}{\hbar} V_{k\ell} \int_0^t d\tau e^{i\omega_{k\ell}\tau} \\ &= -\frac{V_{k\ell}}{E_k - E_\ell} [\exp(i\omega_{k\ell}t) - 1] \\ &= -\frac{2iV_{k\ell} e^{i\omega_{k\ell}t/2}}{E_k - E_\ell} \sin(\omega_{k\ell}t/2) \end{aligned} \quad (2.150)$$

In the last expression, I used the identity $e^{i\theta} - 1 = 2i e^{i\theta/2} \sin(\theta/2)$. Now

$$P_k = |b_k|^2 = \frac{4|V_{k\ell}|^2}{|E_k - E_\ell|^2} \sin^2\left(\frac{\omega_{k\ell}t}{2}\right) \quad (2.151)$$

If we write this using the energy splitting variable we used earlier: $\Delta = (E_k - E_\ell)/2$,

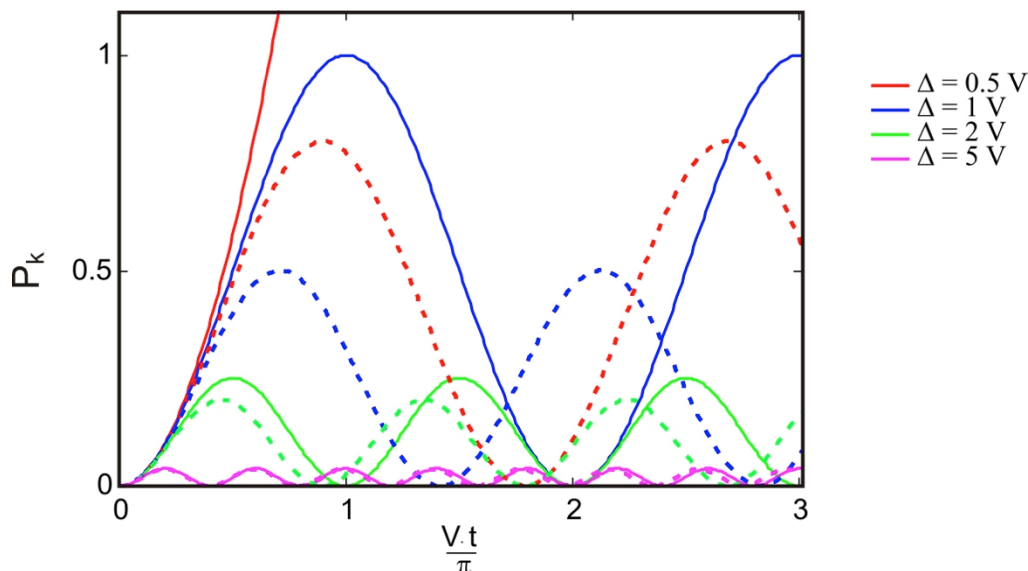
$$P_k = \frac{V^2}{\Delta^2} \sin^2(\Delta t / \hbar) \quad (2.152)$$

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

$$P_k = \frac{V^2}{V^2 + \Delta^2} \sin^2\left(\sqrt{\Delta^2 + V^2} t / \hbar\right) \quad (2.153)$$

As expected, the perturbation theory result works well for $V \ll \Delta$.

Let's examine the time-dependence to P_k , and compare the perturbation theory (solid lines) to the exact result (dashed lines) for different values of Δ .

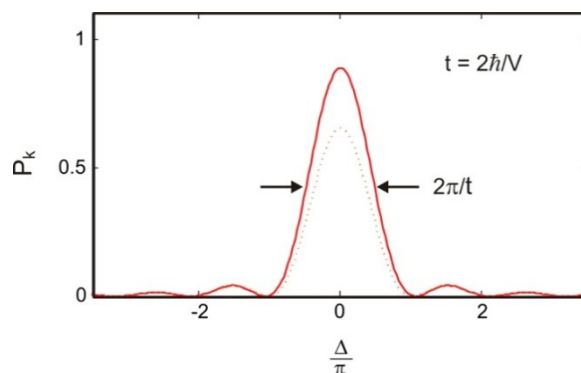


The worst correspondence is for $\Delta=0$ for which the behavior appears quadratic and the probability quickly exceeds unity. It is certainly unrealistic, but we do not expect that the expression will hold for the “strong coupling” case: $\Delta \ll V$. One begins to have quantitative accuracy in for the regime $P_k(t) - P_k(0) < 0.1$ or $\Delta < 4V$.

Now let's look at the dependence on Δ . We can write the first-order result eq. (2.152) as

$$P_k = \frac{V^2 t^2}{\hbar^2} \text{sinc}^2(\Delta t / 2\hbar) \quad (2.154)$$

where $\text{sinc}(x) = \sin(x)/x$. If we plot the probability of transfer from $|\ell\rangle$ to $|k\rangle$ as a function of the energy level splitting ($E_k - E_\ell$) we have:



The probability of transfer is sharply peaked where energy of the initial state matches that of the final state, and the width of the energy mismatch narrows with time. Since $\lim_{x \rightarrow 0} \text{sinc}(x) = 1$, we see that the short time behavior is a quadratic growth in P_k

$$\lim_{\Delta \rightarrow 0} P_k = V^2 t^2 / \hbar^2 \quad (2.155)$$

The integrated area grows linearly with time.

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. A frequency can only be determined as accurately as the length of the time over which you observe oscillations. Since time is not an operator, it is not a true uncertainty relation like $\Delta p \cdot \Delta x \geq 2\pi\hbar$.

In the long time limit, the $\text{sinc}^2(x)$ function narrows to a delta function:

$$\lim_{t \rightarrow \infty} \frac{\sin^2(ax/2)}{ax^2} = \frac{\pi}{2} \delta(x) \quad (2.156)$$

$$\lim_{t \rightarrow \infty} P_k(t) = \frac{2\pi}{\hbar} |V_{k\ell}|^2 \delta(E_k - E_\ell) t \quad (2.157)$$

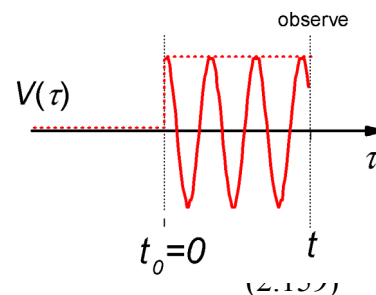
The delta function enforces energy conservation, saying that the energies of the initial and target state must be the same in the long time limit. What is interesting in eq. (2.157) is that we see a probability growing linearly in time. This suggests a transfer *rate* that is independent of time, as expected for simple first-order kinetics:

$$w_k(t) = \frac{\partial P_k(t)}{\partial t} = \frac{2\pi |V_{k\ell}|^2}{\hbar} \delta(E_k - E_\ell) \quad (2.158)$$

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 $dP/dt = -wP$.

Harmonic perturbation

The second model calculation is the interaction of a system with an oscillating perturbation turned on at time $t_0 = 0$. The results will be used to describe how a light field induces transitions in a system through dipole interactions. Again, we are looking to calculate the transition probability between states ℓ and k :



$$V(t) = V \cos \omega t \Theta(t)$$

$$\begin{aligned} V_{k\ell}(t) &= V_{k\ell} \cos \omega t \\ &= \frac{V_{k\ell}}{2} [e^{-i\omega t} + e^{i\omega t}] \end{aligned} \tag{2.160}$$

Setting $t_0 \rightarrow 0$, first-order perturbation theory leads to

$$\begin{aligned} b_k &= \frac{-i}{\hbar} \int_{t_0}^t d\tau V_{k\ell}(\tau) e^{i\omega_{k\ell}\tau} \\ &= \frac{-iV_{k\ell}}{2\hbar} \int_0^t d\tau [e^{i(\omega_{k\ell}-\omega)\tau} + e^{i(\omega_{k\ell}+\omega)\tau}] \\ &= \frac{-iV_{k\ell}}{2\hbar} \left[\frac{e^{i(\omega_{k\ell}-\omega)t} - 1}{\omega_{k\ell} - \omega} + \frac{e^{i(\omega_{k\ell}+\omega)t} - 1}{\omega_{k\ell} + \omega} \right] \end{aligned} \tag{2.161}$$

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

$$b_k = \frac{V_{k\ell}}{\hbar} \left[\frac{e^{i(\omega_{k\ell}-\omega)t/2} \sin[(\omega_{k\ell} - \omega)t/2]}{\omega_{k\ell} - \omega} + \frac{e^{i(\omega_{k\ell}+\omega)t/2} \sin[(\omega_{k\ell} + \omega)t/2]}{\omega_{k\ell} + \omega} \right] \tag{2.162}$$

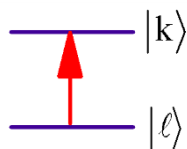
Notice that these terms are only significant when $\omega \approx \omega_{k\ell}$. The condition for efficient transfer is resonance, a matching of the frequency of the harmonic interaction with the energy splitting between quantum states. Consider the resonance conditions that will maximize each of these:

First Term

max at : $\omega = +\omega_{k\ell}$

$$E_k > E_\ell$$

$$E_k = E_\ell + \hbar\omega$$



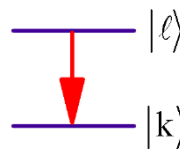
Absorption
(resonant term)

Second Term

$$\omega = -\omega_{k\ell}$$

$$E_k < E_\ell$$

$$E_k = E_\ell - \hbar\omega$$



Stimulated Emission
(anti-resonant term)

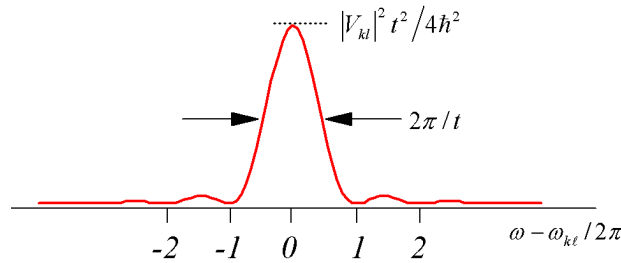
If we consider only absorption, $E_k > E_\ell$, we have:

$$P_{k\ell} = |b_k|^2 = \frac{|V_{k\ell}|^2}{\hbar^2 (\omega_{k\ell} - \omega)^2} \sin^2 \left[\frac{1}{2} (\omega_{k\ell} - \omega) t \right] \quad (2.163)$$

We can compare this with the exact expression:

$$P_{k\ell} = |b_k|^2 = \frac{|V_{k\ell}|^2}{\hbar^2 (\omega_{k\ell} - \omega)^2 + |V_{k\ell}|^2} \sin^2 \left[\frac{1}{2\hbar} \sqrt{|V_{k\ell}|^2 + (\omega_{k\ell} - \omega)^2} t \right]. \quad (2.164)$$

Again, we see that the first-order expression 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 $\omega_{k\ell} = \omega$



Similar to our description of the constant perturbation, the long time limit for this expression leads to a delta function $\delta(\omega_{k\ell} - \omega)$. In this long time limit, we can neglect interferences between the resonant and antiresonant terms. The rates of transitions between k and ℓ states determined from $w_{k\ell} = \partial P_k / \partial t$ becomes

$$w_{k\ell} = \frac{\pi}{2\hbar^2} |V_{k\ell}|^2 \left[\delta(\omega_{k\ell} - \omega) + \delta(\omega_{k\ell} + \omega) \right]. \quad (2.165)$$

We can examine the limitations of this formula. When we look for the behavior on resonance, expanding the $\sin(x)$ shows us that P_k rises quadratically for short times:

$$\lim_{\Delta\omega \rightarrow 0} P_k(t) = \frac{|V_{k\ell}|^2}{4\hbar^2} t^2 \quad (2.166)$$

This clearly will not describe long-time behavior, but it will hold for small P_k , so we require

$$t \ll \frac{2\hbar}{V_{k\ell}} \quad (2.167)$$

At the same time, we cannot observe the system on too short a time scale. We need the field to make several oscillations for this to be considered a harmonic perturbation.

$$t > \frac{1}{\omega} \approx \frac{1}{\omega_{k\ell}} \quad (2.168)$$

$$\text{These relationships imply that we require } V_{k\ell} \ll \hbar\omega_{k\ell}. \quad (2.169)$$

Readings

1. Cohen-Tannoudji, C.; Diu, B.; Lalöe, F., *Quantum Mechanics*. Wiley-Interscience: Paris, 1977; p. 1299.
2. McHale, J. L., *Molecular Spectroscopy*. 1st ed.; Prentice Hall: Upper Saddle River, NJ, 1999; Ch. 4.
3. Sakurai, J. J., *Modern Quantum Mechanics, Revised Edition*. Addison-Wesley: Reading, MA, 1994.