# 2. TIME-EVOLUTION OPERATOR

Our primary interest is with dynamical processes, and for this we need to work with a timedependent 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 we 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 equivalent to Newton's—or more accurately Hamilton's—equations for classical systems. The question is, if we know the wavefunction at time  $t_0$ ,  $|\psi(\mathbf{r},t_0)\rangle$ , how does it change with time? How do we determine  $|\psi(\mathbf{r},t)\rangle$  for some later time  $t > t_0$ ? We will use our intuition here, relying heavily on correspondence to classical mechanics. To simplify notation, in the following discussion we will not explicitly show the spatial dependence of wavefunction.

# Properties of the time-evolution operator

To derive a deterministic equation of motion, we start by asserting *causality*—that  $|\psi(t_0)\rangle$  precedes and determines  $|\psi(t)\rangle$ . As above, we define a "time-displacement operator" or "propagator"  $\hat{U}$  that acts on the wavefunction to the right to propagate the system forward in time from  $t_0$  to t:

$$\left|\psi(t)\right\rangle = \hat{U}(t, t_0) \left|\psi(t_0)\right\rangle \tag{2.1}$$

Additionally, the wavefunction must be continuously differentiable in time, and therefore the state is unchanged when the initial and final time-points are the same

$$\hat{U}(t,t) = 1 \tag{2.2}$$

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 the composition property

$$\hat{U}(t_2, t_0) = \hat{U}(t_2, t_1)\hat{U}(t_1, t_0)$$
(2.3)

Note that since  $\widehat{U}$  acts to the right, order matters:

$$\begin{split} \left| \psi(t_2) \right\rangle &= \hat{U}(t_2, t_1) \hat{U}(t_1, t_0) \left| \psi(t_0) \right\rangle \\ &= \hat{U}(t_2, t_0) \left| \psi(t_1) \right\rangle \end{split}$$
 (2.4)

Equation (2.4) is already very suggestive of an exponential form for  $\hat{U}$ . 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 rather than the absolute initial and final time points:

$$\hat{U}(t_1, t_0) = \hat{U}(t_1 - t_0)$$
(2.5)

As a result of the linearity and the principle of superposition,  $\hat{U}$  is distributive. If we express the state of a system as the superposition

$$\left|\psi\left(t_{0}\right)\right\rangle = a_{1}\left|\varphi_{1}\left(t_{0}\right)\right\rangle + a_{2}\left|\varphi_{2}\left(t_{0}\right)\right\rangle$$

$$(2.6)$$

then

$$\begin{split} |\psi(t)\rangle &= \hat{U}(t,t_{0})|\psi(t_{0})\rangle \\ &= \hat{U}(t,t_{0})a_{1}|\varphi_{1}(t_{0})\rangle + \hat{U}(t,t_{0})a_{2}|\varphi_{2}(t_{0})\rangle \\ &= a_{1}(t)|\varphi_{1}\rangle + a_{2}(t)|\varphi_{2}\rangle \end{aligned}$$
(2.7)

While the coefficient  $a_i(t)$  is typically not equal to  $a_i(t_0)$ , the system must remain properly normalized. That is, the probability amplitude for particles of the system must be conserved,

$$\sum_{n} |a_{n}(t)|^{2} = \sum_{n} |a_{n}(t_{0})|^{2}$$
(2.8)

Thus  $\hat{U}$  is not dependent on  $|\psi\rangle$ , and the differential equation of motion for  $\hat{U}$  is linear in time. Note that eq. implies that  $\hat{U}$  must be unitary.

$$P = \left\langle \psi(t) \middle| \psi(t) \right\rangle = \left\langle \psi(t_0) \middle| \hat{U}^{\dagger} \hat{U} \middle| \psi(t_0) \right\rangle$$
(2.9)

which holds if  $\hat{U}^{\dagger} = \hat{U}^{-1}$ . Also, the inverse of the time-propagator is the time reversal operator. From eq. (2.3):

$$\hat{U}(t,t_0)\hat{U}(t_0,t) = 1$$
(2.10)

$$\therefore \hat{U}^{-1}(t,t_0) = \hat{U}(t_0,t)$$
(2.11)

## An equation of motion for the time-evolution operator

Let's find an equation of motion that describes the time-evolution operator using the change of the system for an *infinitesimal* time-step,  $\delta t : \hat{U}(t + \delta t, t)$ . Since

$$\lim_{\delta t \to 0} \hat{U}(t + \delta t, t) = 1$$
(2.12)

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

$$\hat{U}(t+\delta t) = \hat{U}(t) - i\hat{\Omega}(t)\delta t$$
(2.13)

where  $\hat{\Omega}$  is a time-dependent Hermitian operator, which is required for  $\hat{U}$  to be unitary. We can now write a differential equation for the time-development of  $\hat{U}$  starting with

$$\frac{d\hat{U}(t)}{dt} = \lim_{\delta t \to 0} \frac{\hat{U}(t+\delta t) - \hat{U}(t)}{\delta t}$$
(2.14)

So, from eq. (2.13) we have:

$$\frac{\partial \hat{U}(t,t_0)}{\partial t} = -i\hat{\Omega}\hat{U}(t,t_0)$$
(2.15)

We can now see that the operator needed a complex argument. 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

$$\hat{\Omega} = \frac{\hat{H}}{\hbar} \tag{2.16}$$

With that substitution we have an equation of motion for  $\hat{U}$  :

$$i\hbar \frac{\partial}{\partial t} \hat{U}(t, t_0) = \hat{H} \hat{U}(t, t_0)$$
(2.17)

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

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{H}|\psi\rangle \tag{2.18}$$

If we use the Hamiltonian for a free particle,  $-(\hbar^2/2m)(\partial^2/\partial x^2)$ , we will notice it looks like a classical wave equation except that it's linear in time. Rather, eq. (2.18) looks like a diffusion equation with an imaginary diffusion constant. We are also interested in the equation of motion for  $\hat{U}^{\dagger}$  which describes the time evolution of the conjugate wavefunctions. If we follow the same approach, recognizing that  $\hat{U}^{\dagger}$  acts to the left:

$$\left\langle \psi\left(t\right)\right| = \left\langle \psi\left(t_{0}\right)\right| \hat{U}^{\dagger}\left(t,t_{0}\right)$$
(2.19)

we get

$$-i\hbar\frac{\partial}{\partial t}\hat{U}^{\dagger}(t,t_{0}) = \hat{U}^{\dagger}(t,t_{0})\hat{H}$$
(2.20)

### Evaluating the time-evolution operator

At first glance it may seem straightforward to integrate eq. (2.17). If  $\hat{H}$  is merely a function of time, then

$$\hat{U}(t,t_0) = \exp\left[\frac{-i}{\hbar}\int_{t_0}^t H(t')dt'\right]$$
(2.21)

If we followed our earlier definition of the time-propagator, this exponential would be cast as a series expansion:

$$U(t,t_0)^{?} = 1 - \frac{i}{\hbar} \int_{t_0}^{t} H(t') dt' + \frac{1}{2!} \left(\frac{-i}{\hbar}\right)^{2} \int_{t_0}^{t} \int_{t_0}^{t} dt' dt'' H(t') H(t'') + \dots$$
(2.22)

This approach is dangerous since we are not properly treating  $\hat{H}$  as an operator. Looking at the second term in eq. (2.22), 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  $[\hat{H}(t'), \hat{H}(t'')] = 0$ .

Now, let's proceed a bit more carefully, assuming the Hamiltonians at different times do not commute. Integrating eq. (2.17) directly from  $t_0$  to t gives

$$\hat{U}(t,t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t d\tau \,\hat{H}(\tau) \hat{U}(\tau,t_0)$$
(2.23)

This is the solution; however, it is not very practical since  $\hat{U}(t,t_0)$  is a function of itself. But we can make an iterative expansion by repetitive substitution of  $\hat{U}$  into itself.

The first step in this process is as follows:

$$\hat{U}(t,t_{0}) = 1 - \frac{i}{\hbar} \int_{t_{0}}^{t} d\tau \hat{H}(\tau) \left[ 1 - \frac{i}{\hbar} \int_{t_{0}}^{\tau} d\tau' \hat{H}(\tau') \hat{U}(\tau',t_{0}) \right]$$

$$= 1 + \left( \frac{-i}{\hbar} \right) \int_{t_{0}}^{t} d\tau \hat{H}(\tau) + \left( \frac{-i}{\hbar} \right)^{2} \int_{t_{0}}^{t} d\tau \int_{t_{0}}^{\tau} d\tau' \hat{H}(\tau) \hat{H}(\tau') \hat{U}(\tau',t_{0})$$
(2.24)

Note in the last term of this equation the integration limits enforce a time-ordering; that is, the first integration variable  $\tau'$  must precede the second  $\tau$ . Pictorially, the area of integration is illustrated in Figure 1.



The next substitution step gives

$$\hat{U}(t,t_{0}) = 1 + \left(\frac{-i}{\hbar}\right) \int_{t_{0}}^{t} d\tau \hat{H}(\tau) 
+ \left(\frac{-i}{\hbar}\right)^{2} \int_{t_{0}}^{t} d\tau \int_{t_{0}}^{\tau} d\tau' \hat{H}(\tau) \hat{H}(\tau') 
+ \left(\frac{-i}{\hbar}\right)^{3} \int_{t_{0}}^{t} d\tau \int_{t_{0}}^{\tau} d\tau' \int_{t_{0}}^{\tau'} d\tau'' \hat{H}(\tau) \hat{H}(\tau') \hat{H}(\tau'') \hat{U}(\tau'',t_{0})$$
(2.25)

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

What does this expression represent? Imagine we are starting in state  $|\psi_0\rangle = |\ell\rangle$  and we want to describe how one evolves toward a target state  $t_0$  $|\psi\rangle = |k\rangle$ . The possible paths by which one can shift amplitude and evolve the phase, pictured in terms of  $|\ell\rangle$ these time variables are represented in Figure 2. The first term in eq. (2.25) represents all actions of the Hamiltonian that 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  $\hat{U}$  describes all possible paths between



the 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  $\hat{U}$  is known as the positive time-ordered exponential and is obtained from the iterative substitution

$$\hat{U}(t,t_{0}) = \exp_{+}\left[\frac{-i}{\hbar}\int_{t_{0}}^{t}d\tau \,\hat{H}(\tau)\right]$$

$$= 1 + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar}\right)^{n} \int_{t_{0}}^{t}d\tau_{n} \int_{t_{0}}^{\tau}d\tau_{n} \dots \int_{t_{0}}^{t}d\tau_{1} \,\hat{H}(\tau_{n}) \hat{H}(\tau_{n-1}) \dots \hat{H}(\tau_{1})$$
(2.26)

In this expression the time-ordering of variables can be summarized as

$$\begin{aligned} t_0 &\to \tau_1 \to \tau_2 \to \tau_3 \dots \tau_n \to t \\ t_0 &\to \dots \quad \tau'' \to \tau' \to \tau \end{aligned}$$
 (2.27)

Equation (2.26) tells us how a quantum system evolves over a given time interval. 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.

Now we compare the time-ordered exponential with the traditional expansion of an exponential:

$$1 + \sum_{n=1}^{\infty} \frac{1}{n!} \left(\frac{-i}{\hbar}\right)^n \int_{t_0}^t d\tau_n \dots \int_{t_0}^t d\tau_1 H(\tau_n) H(\tau_{n-1}) \dots H(\tau_1)$$
(2.28)

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. For any expansion term in this series, there are n! possible time-orderings of the  $\tau_n$  time intervals.

We are also interested in the Hermitian conjugate of  $\hat{U}$ , describes motion in eq. (2.20). If we repeat the method above, remembering that  $\hat{U}^{\dagger}(t,t_0)$  acts to the left, then we obtain

$$\hat{U}^{\dagger}(t,t_0) = 1 + \frac{i}{\hbar} \int_{t_0}^t d\tau \, \hat{U}^{\dagger}(t,\tau) \, \hat{H}(\tau)$$
(2.29)

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

$$\hat{U}^{\dagger}(t,t_{0}) = \exp_{-}\left[\frac{i}{\hbar}\int_{t_{0}}^{t}d\tau \,\hat{H}(\tau)\right]$$

$$= 1 + \sum_{n=1}^{\infty} \left(\frac{i}{\hbar}\right)^{n} \int_{t_{0}}^{t}d\tau_{n} \int_{t_{0}}^{\tau_{n}}d\tau_{n-1} \dots \int_{t_{0}}^{\tau_{2}}d\tau_{1}\hat{H}(\tau_{1})\hat{H}(\tau_{2})\dots\hat{H}(\tau_{n})$$
(2.30)

with  $\hat{H}(\tau_i)$  acting to the left.

# Readings

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# 2.2. Integrating the TDSE Directly

How do we evaluate the time-propagator and obtain a time-dependent trajectory for a quantum system? Expressions such as eq. (2.26) are daunting, and there are no simple ways in which to handle them. We can't truncate the exponential because, usually, this is not a rapidly converging series. Also, the solutions oscillate rapidly due to the phase acquired at the energy splitting of the states involved. This leads to a formidable integration problem. Rapid oscillations require small time steps when in fact the dynamics we care about are typically on much longer time scales. For instance, in a molecular dynamics problem, the highest frequency oscillations may be a result of electronically excited states with periods of 1-2 femtoseconds, and the nuclear dynamics that we hope to describe may occur on a 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 the problem and is often an art form. Considerable effort is needed to formulate the problem, particularly in choosing an appropriate basis. 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 they are 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  $\psi_0$ . Then, we can numerically evaluate the time-dependence of the wavefunction over a period t by discretizing time into n small steps of width  $\delta t = \frac{t}{n}$  over which the change of the system is small.

While a variety of strategies can be pursued in practice, one possibility is to expand our wavefunction in the basis set of our choice,

$$\left|\psi(t)\right\rangle = \sum_{n} c_{n}(t) \left|\varphi_{n}\right\rangle \tag{2.31}$$

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

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = \hat{H}|\psi\rangle \tag{2.32}$$

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

$$i\hbar \frac{\partial c_k(t)}{\partial t} = \sum_n H_{kn}(t)c_n(t)$$
(2.33)

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 forward time-step ( $\delta t$ ) is small enough that the Hamiltonian is essentially constant. Then eq. (2.33) becomes

$$i\hbar \,\,\delta c_k(t) = \sum_n H_{kn}(t)c_n(t)\,\delta t \tag{2.34}$$

and the system is propagated as

$$c_k(t+\delta t) = c_k(t) + \delta c_k(t)$$
(2.35)

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

$$\hat{U}(t+\delta t,t) = \exp\left[-\frac{i}{\hbar}\int_{t}^{t+\delta t} dt' \hat{H}(t')\right] \approx \exp\left[-\frac{i}{\hbar}\delta t \hat{H}(t)\right]$$
(2.36)

As illustrated in Figure 3, the time propagator can be written as a product of n propagators over these small intervals,

$$\hat{U}(t) = \lim_{\delta t \to 0} \left[ \hat{U}_n \hat{U}_{n-1} \cdots \hat{U}_2 \hat{U}_1 \right]$$
$$= \lim_{n \to \infty} \prod_{j=0}^{n-1} \hat{U}_j$$
(2.37)

where the time-propagation over the *j*<sup>th</sup> small time step is

$$\hat{U}_{j} = \exp\left[-\frac{i}{\hbar}\delta t \,\hat{H}_{j}\right]$$

$$\hat{H}_{j} = \hat{H}(j\,\delta t)$$
(2.38)

Note that the expressions in eq. (2.37) are operators, time ordered from right to left, denoted with the "+" subscript. Although eq. (2.37) 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  $\delta t$ . In this limit the time propagator does not change much and can be approximated by the short-time expansion



$$\hat{U}_{j} \approx 1 - \frac{i}{\hbar} \delta t \, \hat{H}_{j} \tag{2.39}$$

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

Another complication arises when the potential and kinetic energy operators in the Hamiltonian do not commute. Taking the Hamiltonian to be  $\hat{H} = \hat{T} + \hat{V}$ ,

$$e^{-i\hat{H}(t)\delta t/\hbar} = e^{-i(\hat{T}(t)+\hat{V}(t))\delta t/\hbar}$$

$$\approx e^{-i\hat{T}(t)\delta t/\hbar} e^{-i\hat{V}(t)\delta t/\hbar}$$
(2.40)

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

$$e^{-i\hat{H}(t)\delta t/\hbar} \approx e^{-i\hat{V}(t)\frac{\delta t}{2}/\hbar} e^{-i\hat{T}(t)\delta t/\hbar} e^{-i\hat{V}(t)\frac{\delta t}{2}/\hbar}$$
(2.41)

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

$$e^{\frac{i\hat{V}(j+1)\delta t}{\hbar}}e^{\frac{-i\hat{V}j\delta t}{\hbar}/2} \approx e^{-i\hat{V}j\delta t/\hbar}$$
(2.42)

$$U(t) \approx e^{-i\hat{V}\frac{n\delta t}{2}/\hbar} \left[ \prod_{j=1}^{n} e^{-i\hat{V}j\delta t/\hbar} e^{-i\hat{T}j\delta t/\hbar} \right] e^{-i\hat{V}\frac{\delta t}{2}/\hbar}$$
(2.43)

### Readings

1. Tannor, D. J., *Introduction to Quantum Mechanics: A Time-Dependent Perspective*. University Science Books: Sausilito, 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  $H_0$ , which we can describe exactly, and a time-dependent potential V(t):

$$H = H_0 + V(t) \tag{2.44}$$

The remaining degrees of freedom are discarded, and only enter in the sense that they give rise to the interaction potential with  $H_0$ . This is effective if we 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 eq. (2.44), 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 are

$$H_0 \left| n \right\rangle = E_n \left| n \right\rangle \tag{2.45}$$

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

$$\left|\psi\left(t\right)\right\rangle = \sum_{n} c_{n}\left(t\right) \left|n\right\rangle \tag{2.46}$$

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

$$c_{k}(t) = \left\langle k \left| \psi(t) \right\rangle \right. \tag{2.47}$$

starting with

$$\frac{\partial \left|\psi\right\rangle}{\partial t} = \frac{-i}{\hbar} H \left|\psi\right\rangle \tag{2.48}$$

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

and from eq. (2.49) 
$$= -\frac{i}{\hbar} \sum_{n} \langle k | H | n \rangle c_n(t)$$
(2.50)

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. (2.44), we have:

$$\frac{\partial c_{k}(t)}{\partial t} = -\frac{i}{\hbar} \sum_{n} \left\langle k \left| \left( H_{0} + V(t) \right) \right| n \right\rangle c_{n}(t)$$

$$= -\frac{i}{\hbar} \sum_{n} \left[ E_{n} \delta_{kn} + V_{kn}(t) \right] c_{n}(t)$$
(2.51)

 $\frac{\partial c_k(t)}{\partial t} + \frac{i}{\hbar} E_k c_k(t) = -\frac{i}{\hbar} \sum_n V_{kn}(t) c_n(t)$ (2.52)

Next, we define and substitute

$$c_m(t) = e^{-iE_m t/\hbar} b_m(t)$$
(2.53)

which implies a definition for the wavefunction as

$$\left|\psi\left(t\right)\right\rangle = \sum_{n} b_{n}\left(t\right) e^{-iE_{n}t/\hbar} \left|n\right\rangle$$
(2.54)

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—that is, the time-evolving phase factor, which typically oscillates much faster than the changes to the amplitude of *b* or *c*.



**Figure 4.** Comparison of the time dependent amplitudes c(t) and b(t) of a weakly coupled two-level system, illustrating their fast and slow oscillations, respectively. The mixing angle  $\theta = 0.06\pi$  and  $|V_{k\ell}|/|H_0| = 10^{-4}$ .

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

Now eq. (2.52) becomes

$$e^{-iE_{k}t/\hbar}\frac{\partial b_{k}}{\partial t} = -\frac{i}{\hbar}\sum_{n}V_{kn}(t) e^{-iE_{n}t/\hbar}b_{n}(t)$$
(2.55)

$$i\hbar\frac{\partial b_k}{\partial t} = \sum_n V_{kn}(t) e^{-i\omega_{nk}t} b_n(t)$$
(2.56)

or

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. In matrix notation we write eq. (2.56) as

or,

$$i\hbar\dot{\mathbf{b}} = \mathbf{V}_{t}\mathbf{b} \tag{2.57}$$

where the matrix elements of  $V_I$  (the interaction picture Hamiltonian) are

$$\left[\mathbf{V}_{\mathbf{I}}\right]_{kn} = V_{kn}(t)e^{i\omega_{kn}\tau}$$
(2.58)

Except in simple cases, these equations cannot be solved analytically, but it is often straightforward to integrate numerically, for instance using Runga-Kutta methods.

In a different approach, we can start with the integral solution to eq. (2.58)

$$\mathbf{b} = \mathbf{b}_{\mathbf{0}} - \frac{i}{\hbar} \int_{0}^{t} d\tau \, \mathbf{V}_{\mathbf{I}}(\tau) \mathbf{b}(\tau)$$
(2.59)

For numerical evaluation, we can discretize time into N small intervals of length  $\delta t = \frac{t-t_0}{N}$ , such that  $\delta t \ll \frac{|V|}{\hbar}$ . Under those circumstances we can assume that the terms within the integral in eq. (2.59) are constant over  $\delta t$ , and the integration can be expressed as a summation

$$\mathbf{b}(t) = \mathbf{b}(t_0) - \frac{i}{\hbar} \sum_{j=1}^{N} \mathbf{V}_{\mathbf{I}}(t_{j-1}) \mathbf{b}(t_{j-1}) \delta t$$
  
$$= \mathbf{b}(t_0) - \sum_{j=1}^{N} \delta \mathbf{b}(t_j)$$
(2.60)

Here  $t_j$  is the time at the  $j^{\text{th}}$  time interval  $t_j = j \,\delta t$ . We calculate the expansion coefficients through iterative corrections  $\delta \mathbf{b}$  to the value of the *b* over subsequent time intervals. At any point in time point  $t_j$ , corrections are evaluated using the values of  $V_i$  and *b* at the previous time interval  $t_{j-1}$ . Equation (2.60) implies a recursion relationship relating  $\mathbf{b}(t_j)$  to its value at the previous time interval time interval  $\mathbf{b}(t_{j-1})$ :

$$\mathbf{b}(t_j) = \mathbf{b}(t_{j-1}) \left( 1 - \frac{i}{\hbar} \mathbf{V}_{\mathbf{I}}(t_{j-1}) \delta t \right)$$
(2.61)

In practice this can be evaluated by sequential matrix multiplication and addition, and the value of  $\delta t$  shortened until population is conserved over the course of the calculation. Although this is in essence the method discussed in the previous section, it is a bit more practical in the interactions picture since the integration time step can be much longer for weak external potentials.

When can we use these approaches? 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

$$i\hbar \frac{\partial |\psi_1\rangle}{\partial t} = H_1 |\psi_1\rangle \tag{2.62}$$

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

$$i\hbar|\psi_{0}\rangle\frac{\partial|\psi_{1}\rangle}{\partial t}+i\hbar|\psi_{1}\rangle\frac{\partial|\psi_{0}\rangle}{\partial t}=|\psi_{0}\rangle H_{1}|\psi_{1}\rangle+|\psi_{1}\rangle H_{0}|\psi_{0}\rangle+H_{int}|\psi_{0}\rangle|\psi_{1}\rangle$$
(2.63)

Then, we left operate by  $\langle \psi_1 |$  making use of eq. (2.62),

$$i\hbar \frac{\partial |\psi_0\rangle}{\partial t} = \left[ H_0 + \langle \psi_1 | H_{\rm int} | \psi_1 \rangle \right] |\psi_0\rangle$$
(2.64)

This is equivalent to the TDSE for a Hamiltonian of form (2.44) where the external interaction  $V(t) = \langle \psi_1 | H_{int}(t) | \psi_1 \rangle$  comes from integrating the 1-2 interaction over the sub-space of  $|\psi_1\rangle$ . This represents a time-dependent mean field method.

#### Readings

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# 2.4. Resonant Driving of Two-level System

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

$$V(t) = V \cos \omega t \tag{2.65}$$

$$V_{k\ell}(t) = V_{k\ell} \cos \omega t \tag{2.66}$$

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

We now couple two states  $|a\rangle$  and  $|b\rangle$  with the oscillating field. Here the energy of the states is ordered so that  $\varepsilon_b > \varepsilon_a$ . 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:



$$i\hbar \frac{\partial}{\partial t} b_k(t) = \sum_{n=a,b} b_n(t) V_{kn}(t) e^{-i\omega_{nk}t}$$

$$= \sum_{n=a,b} b_n(t) V_{kn} e^{-i\omega_{nk}t} \cdot \frac{1}{2} \left( e^{-i\omega t} + e^{i\omega t} \right)$$
(2.67)

where cos wt is in its complex form. Writing this explicitly, we get

$$i\hbar\dot{b}_{b} = \frac{1}{2}b_{a}V_{ba}\left[e^{i\left(\omega_{ba}-\omega\right)t} + e^{i\left(\omega_{ba}+\omega\right)t}\right] + \frac{1}{2}b_{b}V_{bb}\left[e^{i\omega t} + e^{-i\omega t}\right]$$
(2.68)

$$i\hbar \dot{b}_a = \frac{1}{2} b_a V_{aa} \left[ e^{i\omega t} + e^{-i\omega t} \right] + \frac{1}{2} b_b V_{ab} \left[ e^{-i(\omega_{ba} + \omega)t} + e^{-i(\omega_{ba} - \omega)t} \right]$$
(2.69)

Note that the expressions in the last term of eq. (2.69) have been rewritten in terms of the positive frequency  $\omega_{ba} = -\omega_{ab}$ . Two of the term in this equation 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 with the form  $\exp[\pm i\omega t]$  or  $\exp[\pm i(\omega_{ba} + \omega)t]$  oscillate very rapidly (relative to  $|V_{ba}|^{-1}$ ) and so do not contribute much to change of  $c_n$  compared to resonant terms of the form  $\exp[\pm i(\omega_{ba} - \omega)t]$ . So now we have

$$\dot{b}_{b} = \frac{-i}{2\hbar} b_{a} V_{ba} e^{i\Delta\omega t}$$
(2.70)

$$\dot{b}_a = \frac{-i}{2\hbar} b_b V_{ab} e^{-i\Delta\omega t}$$
(2.71)

Here the detuning from resonance, the mismatch in the frequencies of the energy gap between states and the frequency of the sinusoidal driving potential, has been defined as

$$\Delta \omega = \omega_{ba} - \omega \tag{2.72}$$

Note that the coefficients are oscillating at the same frequency, but phase shifted with respect to one another.

Now to solve this pair of equations, we begin by differentiating eq. (2.70)

$$\ddot{b}_{b} = \frac{-i}{2\hbar} \Big[ \dot{b}_{a} V_{ba} e^{i\Delta\omega t} + i\Delta\omega b_{a} V_{ba} e^{i\Delta\omega t} \Big]$$
(2.73)

We also rewrite eq. (2.70) as

$$b_a = \frac{2i\hbar}{V_{ba}} \dot{b}_b \ e^{-i\Delta\omega t} \tag{2.74}$$

and substitute eq. (2.71) and eq. (2.74) into eq. (2.73), to give an equation for  $b_b$ :

$$\ddot{b}_{b} - i\Delta\omega\dot{b}_{b} + \frac{|V_{ba}|^{2}}{4\hbar^{2}}b_{b} = 0$$
(2.75)

The second-order differential equation of the form

$$a\ddot{x} + b\dot{x} + cx = 0 \tag{2.76}$$

has the solution

$$x = e^{-(b/2a)t} \left( A \cos \mu t + B \sin \mu t \right)$$
  
$$\mu = \frac{1}{2a} \sqrt{4ac - b^2}$$
 (2.77)

We might notice that this looks the same as the equation for the damped harmonic oscillator, though with an imaginary damping coefficient. Then we find

$$b_b = e^{-i\Delta\omega t/2} \left[ A\cos\Omega_R t + B\sin\Omega_R t \right]$$
(2.78)

where the Rabi Frequency is

$$\Omega_{R} = \frac{1}{2\hbar} \sqrt{|V_{ba}|^{2} + \hbar^{2} (\omega_{ba} - \omega)^{2}}$$
(2.79)

Remembering the initial conditions,  $b_b(0) = 0$  and  $b_a(0) = 1$ , we find

$$P_{b}(t) = |b_{b}(t)|^{2} = \frac{|V_{ba}|^{2}}{|V_{ba}|^{2} + \hbar^{2}(\omega_{ba} - \omega)^{2}} \sin^{2} \Omega_{R} t$$
(2.80)

and that

$$P_a = 1 - P_b \tag{2.81}$$

The amplitude oscillates back and forth between the two states at a frequency dictated by the coupling between them. This is an important observation that we will return to later: electromagnetic fields couple quantum states of matter, creating time-evolving coherences.

Another observation is the importance of *resonance* between the driving potential and the energy splitting between states. Transfer of amplitude from b to a is maximized when the driving field is at the same frequency as the energy splitting between the two states—that is, when the detuning is zero. On resonance, the probability amplitude is driven entirely from one state to another with a frequency  $|V_{ba}|/\hbar$ . The efficiency of driving between a and b states,  $P_{max}$ , drops off with detuning.



# 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. Since operators and wavefunctions can be both be time-dependent, there are different representations of quantum dynamics that emerge. Consider the time-dependence of the expectation value for an operator  $\hat{A}$  starting in the initial state  $\psi_0$ :

$$\begin{split} \left\langle \hat{A}(t) \right\rangle &= \left\langle \psi_0 \left| \hat{U}^{\dagger} \hat{A} \hat{U} \right| \psi_0 \right\rangle \\ &= \left( \left\langle \psi_0 \left| \hat{U}^{\dagger} \right\rangle \hat{A} \left( \hat{U} \left| \psi_0 \right\rangle \right) \quad \rightarrow \left\langle \psi(t) \right| \hat{A} \left| \psi(t) \right\rangle \text{ Schrödinger} \\ &= \left\langle \psi_0 \left| \left( \hat{U}^{\dagger} \hat{A} \hat{U} \right) \right| \psi_0 \right\rangle \quad \rightarrow \left\langle \psi_0 \left| \hat{A}(t) \right| \psi_0 \right\rangle \text{ Heisenberg} \end{split}$$
(2.82)

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

To compare these representations, we can start by defining operators and wavefunctions in the Schrödinger and Heisenberg pictures using eq. ,

$$\langle \hat{A}(t) \rangle = \langle \psi(t) | \hat{A} | \psi(t) \rangle_{s} = \langle \psi | \hat{A}(t) | \psi \rangle_{H}$$
 (2.83)

Here the Heisenberg operator  $\hat{A}_{H}$  is related to the Schrödinger picture operator  $\hat{A}_{S}$  by

$$\begin{array}{l}
A_{H}\left(t\right) = U^{\dagger}\left(t,t_{0}\right)A_{S}U\left(t,t_{0}\right) \\
\hat{A}_{H}\left(t_{0}\right) = \hat{A}_{S}
\end{array}$$
(2.84)

Note, the pictures have the same wavefunction at the reference point  $t_0$ . Since the wavefunction in the Heisenberg picture is time-independent, we can relate the Schrödinger and Heisenberg wavefunctions as

$$\left|\psi_{S}\left(t\right)\right\rangle = \hat{U}\left(t, t_{0}\right)\left|\psi_{H}\right\rangle \tag{2.85}$$

So, 
$$|\psi_{H}\rangle = \hat{U}^{\dagger}(t,t_{0})|\psi_{S}(t)\rangle = |\psi_{S}(t_{0})\rangle$$
 (2.86)

(2.89)

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

$$\hat{A} | \varphi_i \rangle_S = a_i | \varphi_i \rangle_S$$

$$\hat{A}_H | \varphi_i \rangle_H = a_i | \varphi_i \rangle_H$$
(2.87)

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

$$\frac{\partial \hat{A}_{H}}{\partial t} = \frac{\partial}{\partial t} \left( \hat{U}^{\dagger} \hat{A}_{S} \hat{U} \right) = \frac{\partial \hat{U}^{\dagger}}{\partial t} \hat{A}_{S} \hat{U} + \hat{U}^{\dagger} \hat{A}_{S} \frac{\partial \hat{U}}{\partial t} + \hat{U}^{\dagger} \frac{\partial \hat{A}_{S}}{\partial t} \hat{U}$$

$$= \frac{i}{\hbar} \hat{U}^{\dagger} H \hat{A}_{S} \hat{U} - \frac{i}{\hbar} \hat{U}^{\dagger} \hat{A}_{S} H \hat{U} + \left( \frac{\partial \hat{A}}{\partial t} \right)_{H} \qquad (2.88)$$

$$= \frac{i}{\hbar} H_{H} \hat{A}_{H} - \frac{i}{\hbar} \hat{A}_{H} H_{H}$$

$$= -\frac{i}{\hbar} \left[ \hat{A}, H \right]_{H}$$

$$i\hbar \frac{\partial}{\partial t} \hat{A}_{H} = \left[ \hat{A}, H \right]_{H} \qquad (2.89)$$

The result

is known as the Heisenberg equation of motion. We have dropped the last term in eq. (2.88), with the understanding that  $\hat{A}_s$  is independent of time.

An similar equation of motion can be obtained in the Schrödinger picture for the expectation value of the operator. Using  $\langle A(t) \rangle = \langle \psi | \hat{A} | \psi \rangle$  we obtain

$$i\hbar\frac{\partial}{\partial t}\langle\hat{A}(t)\rangle = i\hbar\left[\left\langle\psi\left|\hat{A}\right|\frac{\partial\psi}{\partial t}\right\rangle + \left\langle\frac{\partial\psi}{\partial t}\left|\hat{A}\right|\psi\right\rangle + \left\langle\psi\left|\frac{\partial\hat{A}}{\partial t}\right|\psi\right\rangle\right]$$

$$= \left\langle\left[\hat{A},H\right]\right\rangle + \left\langle\frac{\partial\hat{A}}{\partial t}\right\rangle$$
(2.90)

If  $\hat{A}$  is independent of time (as we expect in the Schrödinger picture), and if it commutes with H, its expectation value does not change with time and it is referred to as a constant of motion.

### 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:

$$H = \frac{p^2}{2m} + V(x)$$
 (2.91)

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

$$\dot{p} = -\frac{\partial V}{\partial x} \tag{2.92}$$

$$\dot{x} = \frac{p}{m}.$$
(2.93)

use of 
$$\left[\hat{x}^{n}, \hat{p}\right] = i\hbar n \hat{x}^{n-1}$$
 (2.94)

$$\left[\hat{x}, \hat{p}^n\right] = i\hbar n \hat{p}^{n-1} \tag{2.95}$$

Curiously, the factors of  $\hbar$  have vanished in eq. (2.92) and eq. (2.93), and quantum mechanics do 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. (2.93) over a time period *t*, we find that the expectation value for the position of the particle follows the classical motion:

$$\langle x(t) \rangle = \frac{\langle p \rangle t}{m} + \langle x(0) \rangle$$
 (2.96)

We can also use the time derivative of eq. (2.93) to obtain an equation that mirrors Newton's second law of motion, F=ma:

$$m\frac{\partial^2 \langle x \rangle}{\partial t^2} = -\langle \nabla V \rangle.$$
(2.97)

These observations underlie Ehrenfest's Theorem, a statement of the classical correspondence of quantum mechanics stating 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.
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- 4. Sakurai, J. J., *Modern Quantum Mechanics, Revised Edition*. Addison-Wesley: Reading, MA, 1994; Ch. 2.

Here, I have made use of

(2.101)

(2.103)

## 2.6. Interaction Picture

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

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t)$$
 (2.98)

where  $\hat{H}_0$  is a Hamiltonian for the degrees of freedom we are interested in, which we treat exactly, and can be a function of time (although it usually won't be for us).  $\hat{V}(t)$  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  $\hat{H}_0$  as a basis set to describe the dynamics induced by  $\hat{V}(t)$ , assuming  $\hat{V}(t)$  is small enough that eigenstates of  $\hat{H}_0$ are a useful basis. If  $\hat{H}_0$  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  $\hat{V}$  to 0, we can see that the time evolution of the exact part of the Hamiltonian  $\hat{H}_0$  is described by

$$\frac{\partial}{\partial t}\hat{U}_{0}(t,t_{0}) = -\frac{i}{\hbar}\hat{H}_{0}(t)\hat{U}_{0}(t,t_{0})$$
(2.99)

where,

$$\hat{U}_{0}(t,t_{0}) = \exp_{+}\left[-\frac{i}{\hbar}\int_{t_{0}}^{t}d\tau \,\hat{H}_{0}(t)\right]$$
(2.100)

or, for a time-independent  $\hat{H}_0$ ,

relative to the slower amplitude changes induced by  $\hat{V}$ .

We define a wavefunction in the interaction picture  $|\psi_{I}\rangle$  in terms of the Schrödinger wavefunction through

 $\left|\psi_{I}\right\rangle = \hat{U}_{0}^{\dagger} \left|\psi_{S}\right\rangle$ 

 $\hat{U}_{0}(t,t_{0}) = e^{-i\hat{H}_{0}(t-t_{0})/\hbar}$ 

$$\left|\psi_{S}\left(t\right)\right\rangle \equiv \hat{U}_{0}\left(t,t_{0}\right)\left|\psi_{I}\left(t\right)\right\rangle$$

$$(2.102)$$

or

Effectively the interaction representation defines wavefunctions in such a way that the phase accumulated under 
$$e^{-i\hat{H}_0 t/\hbar}$$
 is removed. For small  $\hat{V}$ , these are typically high frequency oscillations

Now we need an equation of motion that describes the time evolution of the interaction picture wavefunctions. We begin by substituting eq. (2.102) into the TDSE:

$$i\hbar\frac{\partial}{\partial t}|\psi_{s}\rangle = \hat{H}|\psi_{s}\rangle \tag{2.104}$$

$$\frac{\partial}{\partial t} \hat{U}_{0}(t,t_{0}) |\psi_{I}\rangle = \frac{-i}{\hbar} \hat{H}(t) \hat{U}_{0}(t,t_{0}) |\psi_{I}\rangle$$

$$\frac{\partial \hat{U}_{0}}{\partial t} |\psi_{I}\rangle + \hat{U}_{0} \frac{\partial |\psi_{I}\rangle}{\partial t} = \frac{-i}{\hbar} (\hat{H}_{0} + \hat{V}(t)) \hat{U}_{0}(t,t_{0}) |\psi_{I}\rangle \qquad (2.105)$$

$$\hat{H}_{0} \hat{\mathcal{U}}_{0} |\psi_{I}\rangle + \hat{U}_{0} \frac{\partial |\psi_{I}\rangle}{\partial t} = \frac{-i}{\hbar} (\hat{H}_{0} + \hat{V}(t)) \hat{U}_{0} |\psi_{I}\rangle$$

$$\therefore i\hbar \frac{\partial |\psi_I\rangle}{\partial t} = \hat{V}_I |\psi_I\rangle \qquad (2.106)$$

where

<u>-i</u> ħ

$$\hat{V}_{I}(t) = \hat{U}_{0}^{\dagger}(t, t_{0}) \hat{V}(t) \hat{U}_{0}(t, t_{0})$$
(2.107)

We see that  $|\psi_I\rangle$  satisfies the Schrödinger equation with a new Hamiltonian in eq. (2.107)—the interaction picture Hamiltonian,  $\hat{V}_I(t)$ . We have performed a unitary transformation of  $\hat{V}(t)$  into the frame of reference of  $\hat{H}_0$ , using  $\hat{U}_0$ . Note that the matrix elements of  $\hat{V}_I$  are  $\langle k | \hat{V}_I | l \rangle = e^{-i\omega_{lk}t} V_{kl}$  where k and l are eigenstates of  $\hat{H}_0$ .

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

$$\left|\psi_{I}(t)\right\rangle = \hat{U}_{I}(t,t_{0})\left|\psi_{I}(t_{0})\right\rangle$$

$$(2.108)$$

where

$$\hat{U}_{I}(t,t_{0}) = \exp_{+}\left[\frac{-i}{\hbar}\int_{t_{0}}^{t}d\tau \,\hat{V}_{I}(\tau)\right]$$
(2.109)

Now we see that

$$\begin{split} \left| \psi_{s}(t) \right\rangle &= \hat{U}_{0}(t,t_{0}) \left| \psi_{I}(t) \right\rangle \\ &= \hat{U}_{0}(t,t_{0}) \hat{U}_{I}(t,t_{0}) \left| \psi_{I}(t_{0}) \right\rangle \\ &= \hat{U}_{0}(t,t_{0}) \hat{U}_{I}(t,t_{0}) \left| \psi_{S}(t_{0}) \right\rangle \\ &\therefore \quad \hat{U}(t,t_{0}) &= \hat{U}_{0}(t,t_{0}) \hat{U}_{I}(t,t_{0}) \end{split}$$
(2.111)

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

$$\hat{U}^{\dagger}(t,t_{0}) = \hat{U}_{I}^{\dagger}(t,t_{0})\hat{U}_{0}^{\dagger}(t,t_{0}) = \exp_{-}\left[\frac{i}{\hbar}\int_{t_{0}}^{t}d\tau \,\hat{V}_{I}(\tau)\right]\exp_{-}\left[\frac{i}{\hbar}\int_{t_{0}}^{t}d\tau \,\hat{H}_{0}(\tau)\right]$$
(2.112)

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  $\hat{U}$  in eq.(2.111) by using eq. (2.109):

$$\hat{U}(t,t_{0}) = \hat{U}_{0}(t,t_{0}) + \left(\frac{-i}{\hbar}\right) \int_{t_{0}}^{t} d\tau \,\hat{U}_{0}(t,\tau) \hat{V}(\tau) \hat{U}_{0}(\tau,t_{0}) + \cdots \\
= \hat{U}_{0}(t,t_{0}) + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar}\right)^{n} \int_{t_{0}}^{t} d\tau_{n} \int_{t_{0}}^{\tau_{n}} d\tau_{n-1} \dots \int_{t_{0}}^{\tau_{2}} d\tau_{1} \,\hat{U}_{0}(t,\tau_{n}) \hat{V}(\tau_{n}) \hat{U}_{0}(\tau_{n},\tau_{n-1}) \dots \quad (2.113) \\
\times \hat{U}_{0}(\tau_{2},\tau_{1}) \,\hat{V}(\tau_{1}) \hat{U}_{0}(\tau_{1},t_{0})$$

Here we have used the composition property of  $\hat{U}(t,t_0)$ . The same positive time-ordering applies. Note that the interactions  $\hat{V}(\tau_i)$  are not in the interaction representation here. Rather we used the definition in eq. (2.107) and collected terms. Now consider how  $\hat{U}$  describes the time-dependence

if we initiate the system in an eigenstate of  $\hat{H}_0 |l\rangle$  and observe the amplitude in a target eigenstate  $|k\rangle$ . The system evolves in eigenstates of  $\hat{H}_0$  during the different time periods, with the time-dependent interactions V driving the transitions between these states. As illustrated in Figure 8, the first-order term describes direct transitions between  $|l\rangle$  and  $|k\rangle$  induced by  $\hat{V}$ , integrated over the full time-period. Before the interaction phase is acquired as  $e^{-iE_{\ell}(\tau-t_0)/\hbar}$ , whereas after the interaction phase is acquired as  $e^{-iE_{\ell}(\tau-\tau)/\hbar}$ . Higher-order terms in the timeordered exponential account for all possible intermediate pathways.



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

$$\begin{split} \left\langle \hat{A}(t) \right\rangle &= \left\langle \psi(t) \left| \hat{A} \right| \psi(t) \right\rangle \\ &= \left\langle \psi(t_0) \left| \hat{U}^{\dagger}(t, t_0) \hat{A} \hat{U}(t, t_0) \right| \psi(t_0) \right\rangle \\ &= \left\langle \psi(t_0) \left| \hat{U}^{\dagger}_I \hat{U}^{\dagger}_0 \hat{A} \hat{U}_0 \hat{U}_I \right| \psi(t_0) \right\rangle \\ &= \left\langle \psi_I(t) \left| \hat{A}_I \right| \psi_I(t) \right\rangle \\ \hat{A}_I &= \hat{U}^{\dagger}_0 \hat{A}_S \hat{U}_0 \end{split}$$
(2.115)

where

We also

So, the operators in the interaction picture also evolve in time, but under  $\hat{H}_0$ . This can be expressed as a Heisenberg equation by differentiating  $\hat{A}_i$ :

$$\frac{\partial}{\partial t}\hat{A}_{I} = \frac{i}{\hbar} \Big[\hat{H}_{0}, \hat{A}_{I}\Big]$$
(2.116)

know 
$$\frac{\partial}{\partial t} |\psi_{I}\rangle = \frac{-i}{\hbar} \hat{V}_{I}(t) |\psi_{I}\rangle \qquad (2.117)$$

Notice that the interaction representation is a partition between the Schrödinger and Heisenberg representations. Wavefunctions evolve under  $\hat{V}_{I}$ , while operators evolve under  $\hat{H}_{0}$ .

For 
$$\hat{H}_0 = 0$$
,  $\hat{V}(t) = \hat{H} \implies \frac{\partial A}{\partial t} = 0$ ;  $\frac{\partial}{\partial t} |\psi_s\rangle = \frac{-i}{\hbar} \hat{H} |\psi_s\rangle$  Schrödinger  
For  $\hat{H}_0 = \hat{H}$ ,  $\hat{V}(t) = 0 \implies \frac{\partial \hat{A}}{\partial t} = \frac{i}{\hbar} [\hat{H}, \hat{A}]$ ;  $\frac{\partial \psi}{\partial t} = 0$  Heisenberg (2.118)

# The relationship between $\hat{U}_I$ and $b_n$

Earlier we described how time-dependent problems with Hamiltonians of the form  $\hat{H} = \hat{H}_0 + \hat{V}(t)$  could be solved in terms of the time-evolving amplitudes in the eigenstates of  $\hat{H}_0$ . We can describe the state of the system as a superposition

$$\left|\psi\left(t\right)\right\rangle = \sum_{n} c_{n}\left(t\right)\left|n\right\rangle \tag{2.119}$$

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

$$c_{k}(t) = \langle k | \psi(t) \rangle = \langle k | \hat{U}(t, t_{0}) | \psi(t_{0}) \rangle$$
  
$$= \langle k | \hat{U}_{0} \hat{U}_{I} | \psi(t_{0}) \rangle$$
  
$$= e^{-iE_{k}t/\hbar} \langle k | \hat{U}_{I} | \psi(t_{0}) \rangle$$
  
(2.120)

Now, comparing eq. (2.120) and (2.53) allows us to recognize that our earlier modified expansion coefficients  $b_n$  were expansion coefficients for interaction picture wavefunctions

$$b_{k}(t) = \left\langle k \left| \psi_{I}(t) \right\rangle = \left\langle k \left| \hat{U}_{I} \right| \psi(t_{0}) \right\rangle$$
(2.121)

#### Readings

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# 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 our 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):

$$\left|\psi_{I}(t)\right\rangle = \sum_{n} b_{n}(t) \left|n\right\rangle \tag{2.122}$$

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

$$b_{k} = \left\langle k \left| U_{I}\left(t, t_{0}\right) \right| \psi\left(t_{0}\right) \right\rangle$$
(2.123)

where

$$U_{I}(t,t_{0}) = \exp_{+}\left[\frac{-i}{\hbar}\int_{t_{0}}^{t}V_{I}(\tau)d\tau\right]$$
(2.124)

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

Expanding gives us

$$b_{k}(t) = \left\langle k \left| \exp_{+} \left[ -\frac{i}{\hbar} \int_{t_{0}}^{t} d\tau V_{I}(\tau) \right] \right| \ell \right\rangle$$
(2.125)

$$b_{k}(t) = \langle k | \ell \rangle - \frac{i}{\hbar} \int_{t_{0}}^{t} d\tau \langle k | V_{I}(\tau) | \ell \rangle + \left(\frac{-i}{\hbar}\right)^{2} \int_{t_{0}}^{t} d\tau_{2} \int_{t_{0}}^{\tau_{2}} d\tau_{1} \langle k | V_{I}(\tau_{2}) V_{I}(\tau_{1}) | \ell \rangle + \dots$$

$$(2.126)$$

now, using

 $\left\langle k \left| V_{I}(t) \right| \ell \right\rangle = \left\langle k \left| U_{0}^{\dagger} V(t) U_{0} \right| \ell \right\rangle = e^{-i\omega_{\ell k} t} V_{k \ell}(t)$ (2.127)

we obtain

$$b_k(t) = \delta_{k\ell} - \frac{i}{\hbar} \int_{t_0}^t d\tau_1 \, e^{-i\omega_{\ell k} \tau_1} V_{k\ell}(\tau_1) \qquad \text{``first-order''} \qquad (2.128)$$

+ 
$$\sum_{m} \left(\frac{-i}{\hbar}\right)^{2} \int_{t_{0}}^{t} d\tau_{2} \int_{t_{0}}^{\tau_{2}} d\tau_{1} e^{-i\omega_{mk}\tau_{2}} V_{km}(\tau_{2}) e^{-i\omega_{\ell m}\tau_{1}} V_{m\ell}(\tau_{1})$$
 "second-order" (2.129)  
+...

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, which we would extend a calculation, should be evaluated initially by which allowed pathways between  $|\ell\rangle$  and  $|k\rangle$  we need to account for, and which ones are allowed by the matrix elements.

For first-order perturbation theory, the expression in eq. (2.128) is the solution to the differential equation that we get for direct coupling between  $|\ell\rangle$  and  $|k\rangle$ :

$$\frac{\partial}{\partial t}b_{k} = \frac{-i}{\hbar} e^{-i\omega_{\ell k}t} V_{k\ell}(t) b_{\ell}(0)$$
(2.130)

This indicates that the solution does not allow for the feedback between  $|\ell\rangle$  and  $|k\rangle$ , which 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

$$b_{k}(t) = \sum_{n} b_{n}(0) \langle k | U_{I} | n \rangle$$
(2.131)

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  $\omega_{\ell k}$ :

$$b_{k}(t) = -\frac{i}{\hbar} \int_{-\infty}^{+\infty} d\tau \ e^{-i\omega_{lk}\tau} V_{k\ell}(\tau)$$
(2.132)

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

$$\tilde{V}(\omega) \equiv \tilde{\mathcal{F}}\left[V(t)\right] = \int_{-\infty}^{+\infty} dt \, V(t) \exp(i\omega t)$$
(2.133)

$$V(t) = \tilde{\mathcal{F}}^{-1} \Big[ \tilde{V}(\omega) \Big] = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \, \tilde{V}(\omega) \exp(-i\omega t)$$
(2.134)

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

$$P_{k\ell} = \frac{2\pi \left| \tilde{V}_{k\ell} \left( \omega_{k\ell} \right) \right|^2}{\hbar^2}$$
(2.135)



Figure 9

## **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, we write the complete time-dependent Hamiltonian:

$$H(t) = T + V(t) = \frac{p^2}{2m} + \frac{1}{2}k(t)x^2$$
(2.136)

Now, we 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 as follows:

$$k(t) = k_0 + \delta k(t) \quad k_0 = m\Omega^2$$
  
$$\delta k(t) = \delta k_0 \exp\left(-\frac{(t-t_0)^2}{2\sigma^2}\right) \qquad (2.137)$$

$$H = \underbrace{\frac{p^2}{2m} + \frac{1}{2}k_0x^2}_{H_0} + \underbrace{\frac{1}{2}\delta k_0x^2 \exp\left(-\frac{(t-t_0)^2}{2\sigma^2}\right)}_{V(t)}$$
(2.138)

where  $\delta k_0$  is the magnitude of the induced change in the force constant, and  $\sigma$  is the time-width of the Gaussian perturbation. So, we know the eigenstates of  $H_0$ :  $H_0 | n \rangle = E_n | n \rangle$ 

$$H_{0} = \hbar \Omega \left( a^{\dagger} a + \frac{1}{2} \right)$$
$$E_{n} = \hbar \Omega \left( n + \frac{1}{2} \right)$$
(2.139)

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 
$$n \neq 0$$
:  $b_n(t) = \frac{-i}{\hbar} \int_{t_0}^t d\tau \ V_{n0}(\tau) \ e^{i\omega_{n0}\tau}$  (2.140)

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

$$b_n(t) = \frac{-i}{2\hbar} \delta k_0 \left\langle n \left| x^2 \right| 0 \right\rangle \int_{-\infty}^{+\infty} d\tau \ e^{in\Omega\tau} e^{-\tau^2/2\sigma^2}$$
(2.141)

which leads to

$$b_n(t) = \frac{-i}{2\hbar} \,\delta k_0 \sqrt{2\pi} \sigma \left\langle n \left| x^2 \right| 0 \right\rangle e^{-n^2 \sigma^2 \Omega^2 / 2} \tag{2.142}$$

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

$$\int_{-\infty}^{+\infty} \exp\left(ax^2 + bx + c\right) dx = \sqrt{\frac{-\pi}{a}} \exp\left(c - \frac{1}{4}\frac{b^2}{a}\right)$$
(2.143)

$$\int_{-\infty}^{+\infty} \exp\left(-ax^2 + ibx\right) dx = \sqrt{\frac{\pi}{a}} \exp\left(-\frac{b^2}{4a}\right)$$
(2.144)

What about the matrix element?

$$x^{2} = \frac{\hbar}{2m\Omega} \left( a + a^{\dagger} \right)^{2} = \frac{\hbar}{2m\Omega} \left( aa + a^{\dagger}a + aa^{\dagger} + a^{\dagger}a^{\dagger} \right)$$
(2.145)

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

$$\left\langle 2\left|x^{2}\right|0\right\rangle = \sqrt{2}\frac{\hbar}{2m\Omega}$$
(2.146)

$$b_2 = \frac{-i\sqrt{\pi}\,\delta k_0\,\sigma}{2m\Omega}\,e^{-2\sigma^2\Omega^2} \tag{2.147}$$

so,

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

$$P_{2} = \left| b_{2} \right|^{2} = \frac{\pi \delta k_{0}^{2} \sigma^{2}}{2m^{2} \Omega^{2}} e^{-4\sigma^{2} \Omega^{2}}$$
(2.148)

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

$$\sigma \ll \frac{1}{\Omega} \tag{2.149}$$

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,  $\sigma\Omega >> 1$ , 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 rewrite eq. (2.148) as

$$P_2 = \left(\sigma\Omega\right)^2 \left(\frac{\delta k_0}{k_0}\right)^2 \frac{\pi}{2} e^{-4\left(\sigma\Omega\right)^2}$$
(2.150)

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

$$\left(\sigma\Omega\right)\left(\frac{\delta k_0}{k_0}\right) <<1$$
(2.151)

Generally, the first order result will hold when the magnitude of the perturbation  $\delta k_0$  is small compared to  $k_0$ , even if  $\sigma \approx \Omega^{-1}$ .

#### One step further...

The preceding example was simple, but it tracks the general approach to setting up problems that we treat with time-dependent perturbation theory. The approach relies on writing a Hamiltonian that can be cast into a Hamiltonian that we 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

$$V(x) = \frac{1}{2!} \frac{\partial^2 V}{\partial x^2} \bigg|_{x=0} x^2 + \frac{1}{2!} \frac{\partial^2 V}{\partial x \partial y} \bigg|_{x=0} xy + \frac{1}{3!} \sum_{y,z} \frac{\partial^3 V}{\partial x \partial y \partial z} \bigg|_{x=0} xyz + \cdots$$

$$= \frac{1}{2} kx^2 + V^{(2)} xy + \left(V_3^{(3)} x^3 + V_2^{(3)} x^2 y + V_1^{(3)} xy^2\right) + \cdots$$
(2.152)

The first term is the harmonic force constant for *x*, and the second term is a bilinear coupling whose magnitude  $V^{(2)}$  indicates how much a change in the variable *y* influences the variable *x*. This cross

term normally disappears in a normal mode transformation. The remaining  $V^{(3)}$  terms are cubic expansion terms.  $V_0^{(3)}$  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  $V_1^{(3)}$  term, so that  $\delta k_0/2 = V_2^{(3)}$ , and giving the value of y a time-dependence described by the Gaussian waveform. If we consider matrix elements in the other cubic terms, we recognize that terms such as  $V_2^{(3)}$  in the above example will give rise to single quantum excitations from  $|0\rangle$  to  $|1\rangle$  not present in our earlier solution.

### Readings

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# 2.8. Fermi's Golden Rule

Several important relationships in quantum mechanics that describe rate processes come from firstorder 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  $t_0$ :

$$V(t) = V \Theta(t - t_0) = \begin{cases} 0 & t < t_0 \\ V & t \ge t_0 \end{cases}$$
(2.153)

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



$$b_{k} = -\frac{i}{\hbar} \int_{t_{0}}^{t} d\tau \ e^{i\omega_{k\ell}(\tau - t_{0})} V_{k\ell}(\tau)$$

$$(2.154)$$

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

$$b_{k} = -\frac{i}{\hbar} V_{k\ell} \int_{0}^{t} d\tau \ e^{i\omega_{k\ell}\tau}$$

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

$$= -\frac{2iV_{k\ell}}{E_{k} - E_{\ell}} \sin(\omega_{k\ell}t/2)$$
(2.155)

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

$$P_{k} = \left|b_{k}\right|^{2} = \frac{4\left|V_{k\ell}\right|^{2}}{\left|E_{k} - E_{\ell}\right|^{2}} \sin^{2}\left(\frac{\omega_{k\ell}t}{2}\right)$$
(2.156)

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

$$P_k = \frac{V^2}{\Delta^2} \sin^2\left(\Delta t \,/\,\hbar\right) \tag{2.157}$$

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

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$$P_{k} = \frac{V^{2}}{V^{2} + \Delta^{2}} \sin^{2} \left( \sqrt{\Delta^{2} + V^{2}} t \,/\, \hbar \right)$$
(2.158)

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  $\Delta$ .



The worst correspondence is for  $\Delta = 0$ , for which the behavior appears quadratic and the probability quickly exceeds unity. It's certainly unrealistic, but we don't 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 plot this a little differently, scaling the time axis as  $2\pi\hbar/\Delta$ , focusing on the changes for  $t \ll \Delta/\hbar$ , and instead looking at  $\sqrt{P_k} = |\mathbf{b}_k|$ .



Here we see that the first order perturbation theory result is excellent as describing the initial changes as amplitude flows into the target state  $|k\rangle$ , particularly for small changes  $|b_k(t)|^2 < 0.1$ .

Now let's look at how the efficiency of transfer depends on  $\Delta$  and t. We can write the first-order result eq. (2.157) as

$$P_{k} = \frac{V^{2}t^{2}}{\hbar^{2}}\operatorname{sinc}^{2}\left(\Delta \cdot t / 2\hbar\right)$$
(2.159)

where  $sinc(x) = \frac{sin(x)}{x}$ , and plot the probability of transfer from  $|\ell\rangle$  to  $|k\rangle$  in Figure 14:



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  $\lim_{x\to 0} \operatorname{sinc}(x) = 1$ , we see that the short time behavior is a quadratic growth in  $P_k$ 

$$\lim_{\Delta \to 0} P_k = V^2 t^2 / \hbar^2$$
 (2.160)

The integrated area grows linearly with time. These are clearly non-physical results and serve to illustrate that first-order perturbation theory only applies for small changes in amplitude and for times when feedback of the amplitude back into the initial state isn't significant.

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  $\Delta E \cdot \Delta t \ge 2\pi\hbar$ . However, remember that this is 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 we observe oscillations. Since time is not an operator, it is not a true quantum uncertainly relation like  $\Delta p \cdot \Delta x \ge 2\pi\hbar$ , which derives from the fact that *p* and *x* do not commute.

In the long-time limit, the  $sinc^2(x)$  function narrows to a delta function:

$$\lim_{t \to \infty} \frac{\sin^2\left(ax/2\right)}{ax^2} = \frac{\pi}{2} \,\delta(x) \tag{2.161}$$

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$$\lim_{t \to \infty} P_k(t) = \frac{2\pi}{\hbar} |V_{k\ell}|^2 \,\delta(E_k - E_\ell) t \tag{2.162}$$

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. (2.162) 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:

$$w_{k}(t) = \frac{\partial P_{k}(t)}{\partial t} = \frac{2\pi |V_{k\ell}|^{2}}{\hbar} \delta(E_{k} - E_{\ell})$$
(2.163)

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 we 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  $\ell$  and k:

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

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

$$= \frac{V_{k\ell}}{2} \left[ e^{-i\omega t} + e^{i\omega t} \right]$$

$$(2.164) \qquad V(t)$$

$$(2.165) \qquad t_0 = 0 \qquad t$$
Figure 15

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

$$b_{k} = \frac{-i}{\hbar} \int_{t_{0}}^{t} d\tau V_{k\ell}(\tau) e^{i\omega_{k\ell}\tau}$$

$$= \frac{-iV_{k\ell}}{2\hbar} \int_{0}^{t} d\tau \left[ e^{i(\omega_{k\ell}-\omega)\tau} + e^{i(\omega_{k\ell}+\omega)\tau} \right]$$

$$= \frac{-iV_{k\ell}}{2\hbar} \left[ \frac{e^{i(\omega_{k\ell}-\omega)t} - 1}{\omega_{k\ell}-\omega} + \frac{e^{i(\omega_{k\ell}+\omega)t} - 1}{\omega_{k\ell}+\omega} \right]$$
(2.166)

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

$$b_{k} = \frac{V_{k\ell}}{\hbar} \left[ \frac{e^{i(\omega_{k\ell} - \omega)t/2} \sin\left[(\omega_{k\ell} - \omega)t/2\right]}{\omega_{k\ell} - \omega} + \frac{e^{i(\omega_{k\ell} + \omega)t/2} \sin\left[(\omega_{k\ell} + \omega)t/2\right]}{\omega_{k\ell} + \omega} \right]$$
(2.167)

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:



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

$$P_{k\ell} = \left|b_k\right|^2 = \frac{\left|V_{k\ell}\right|^2}{\hbar^2 \left(\omega_{k\ell} - \omega\right)^2} \quad \sin^2 \left[\frac{1}{2} \left(\omega_{k\ell} - \omega\right) t\right]$$
(2.168)

which we can compare with the exact expression

$$P_{k\ell} = |b_k|^2 = \frac{|V_{k\ell}|^2}{\hbar^2 (\omega_{k\ell} - \omega)^2 + |V_{k\ell}|^2} \quad \sin^2 \left[ \frac{1}{2} \sqrt{\frac{|V_{k\ell}|^2}{\hbar^2} + (\omega_{k\ell} - \omega)^2} t \right]$$
(2.169)

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



Like 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  $\ell$  states determined from  $w_{k\ell} = \partial P_k / \partial t$  becomes

$$w_{k\ell} = \frac{\pi}{2\hbar^2} |V_{k\ell}|^2 \left[ \delta(\omega_{k\ell} - \omega) + \delta(\omega_{k\ell} + \omega) \right]$$
(2.170)

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:

$$\lim_{\Delta\omega\to 0} P_k(t) = \frac{|V_{k\ell}|^2}{4\hbar^2} t^2$$
(2.171)

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

$$t \ll \frac{2\hbar}{V_{k\ell}} \tag{2.172}$$

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

$$t > \frac{1}{\omega} \approx \frac{1}{\omega_{k\ell}} \tag{2.173}$$

These relationships imply that we require  $V_{k\ell} \ll \hbar \omega_{k\ell}$ . (2.174)

## Readings

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