Chapter 16

The shadow whispered warning, but the darkness promised sanctuary so he embraced it. He layered himself into the wall, and pierced the night with the glower of a sentry just attacked. The three men appeared. He remained a frozen gargoyle in the brick. They strode straight at him, unwavering, shoulder to shoulder, the short one in the middle. It couldn’t be...but it was...and there were two big hands on his biceps as the short one mumbled “Fermi wants to see you,” turned and lead, as his jailors ensured he followed.

Time-Dependent Perturbation Theory (TDPT)

Semiclassical Strategy

Without explicit time dependence in the Hamiltonian, the time-evolution is simply a matter of phase, i.e.,

\[ |\psi(t)> = |\psi(0)> e^{-iE_n t/\hbar}, \]

where the exponential is a phase factor. If this is the only time dependence, transitions do not occur. Consider the hydrogen atom. If an electron is in the excited state \( n, 0, 0 > = |2, 0, 0>, \) time evolution of the system is determined by

\[ |\psi_{2,0,0}(t)> = |\psi_{2,0,0}(0)> e^{-iE_2 t/\hbar}, \]

and nothing will cause it to decay to the ground state. A geometric interpretation would be that as time advances, only the “direction” of the phase factor changes. The last equation describes an electron that would remain in the excited state forever. We know, in fact, that the electron will decay to the ground state.

This description does not include electromagnetic coupling. And we will say this only once because it is generally beyond our scope, if there were no vacuum flucuations, the electron would stay in an excited state forever. The complete way to treat this is with relativisitic quantum field theory. Another satisfactory way for a specific class of problems is to treat the particles with quantum mechanics and the electromagnetic fields classically with Maxwell’s equations. Using this semiclassical treatment, the effect of the radiation field on the particles can be correctly described (although the effect of the radiation field on the particle cannot).

Time-Dependent Perturbation Theory

The time-dependent Schrodinger equation is

\[ \mathcal{H} |\psi(t)> = i\hbar \frac{d}{dt} |\psi(t)> . \]

To this point \( \mathcal{H} \neq \mathcal{H}(t). \) This leads to stationary states or “quantum statics,” where atomic transitions do not occur and time evolution is described only by changes in phase. If \( \mathcal{H} = \mathcal{H}(t), \) we need a different approach. We make a key assumption—we assume that: the time-dependent part of the Hamiltonian is small compared to the time-independent part.
Symbolically, this means that
\[ \mathcal{H}(t) = \mathcal{H}_0 + \mathcal{H}_1(t), \]
where the effects of \( \mathcal{H}_1(t) \) are much less than the effects of \( \mathcal{H}_0 \). For atomic physics, we might interpret this statement as the effects of the electromagnetic field of a photon is small compared to the effects of the electrostatic field inside an atom.

Satisfactory results from this approach assume we know the solution to
\[ \mathcal{H}_0 |n\rangle = E_n |n\rangle, \]
the time independent portion of the problem. A general solution is a superposition of all stationary states, i.e.,
\[ |\phi(t)\rangle = \sum_{n} a_n |n\rangle e^{-iE_n t/\hbar}, \]
where \( |n\rangle \) is an orthonormal basis such that \( \langle n | m \rangle = \delta_{n,m} \), and we write the wave function as \( \phi(t) \) to distinguish the simple time dependence where \( \mathcal{H} \neq \mathcal{H}(t) \) from wave functions \( \psi(t) \) which will represent \( \mathcal{H} = \mathcal{H}(t) \). In light of the current discussion, we could write the coefficients \( a_n(0) \) vice \( a_n \). When \( \mathcal{H} = \mathcal{H}(t) \), or equivalently when \( \mathcal{H}_1(t) \neq 0 \), we expect the solution to the time dependent problem to be,
\[ \langle \mathcal{H}_0 + \mathcal{H}_1 \rangle |\psi(t)\rangle = i\hbar \frac{d}{dt} |\psi(t)\rangle, \]
where the time dependence is denoted implicitly \( \mathcal{H}_1(t) = \mathcal{H}_1 \), as is the usual convention. We expect a solution of the form
\[ |\psi(t)\rangle = \sum_{n} a_n(t) |n\rangle e^{-iE_n t/\hbar}. \]
Note that equation (18–2) is independent of representation. Using expansion (18–2) in equation (18–1),
\[ \mathcal{H}_0 \sum_{n} a_n(t) |n\rangle e^{-iE_n t/\hbar} = \frac{i\hbar}{\hbar} d a_n(t) dt \]
\[ \mathcal{H}_1 \sum_{n} a_n(t) |n\rangle e^{-iE_n t/\hbar} \]
\[ \Rightarrow \sum_{n} \mathcal{H}_0 a_n(t) |n\rangle e^{-iE_n t/\hbar} + \sum_{n} \mathcal{H}_1 a_n(t) |n\rangle e^{-iE_n t/\hbar} \]
\[ \Rightarrow \sum_{n} \mathcal{H}_0 a_n(t) |n\rangle e^{-iE_n t/\hbar} + \sum_{n} \mathcal{H}_1 a_n(t) |n\rangle e^{-iE_n t/\hbar} \]
\[ \Rightarrow \sum_{n} \mathcal{H}_0 a_n(t) |n\rangle e^{-iE_n t/\hbar} + \sum_{n} \mathcal{H}_1 a_n(t) |n\rangle e^{-iE_n t/\hbar} \]
\[ \Rightarrow \sum_{n} \mathcal{H}_0 a_n(t) |n\rangle e^{-iE_n t/\hbar} + \sum_{n} \mathcal{H}_1 a_n(t) |n\rangle e^{-iE_n t/\hbar} \]
\[ \Rightarrow \sum_{n} \mathcal{H}_0 a_n(t) |n\rangle e^{-iE_n t/\hbar} + \sum_{n} \mathcal{H}_1 a_n(t) |n\rangle e^{-iE_n t/\hbar} \]
\[ \sum_n a_n(t)E_n j_n > e^{-iE_nt/\hbar} + \sum_n \mathcal{H}_1 a_n(t) j_n > e^{-iE_nt/\hbar} \]
\[ = \sum_n i\hbar \frac{d}{dt} a_n(t) j_n > e^{-iE_nt/\hbar} + \sum_n a_n(t)E_n j_n > e^{-iE_nt/\hbar} \]
\[ \Rightarrow \sum_n \mathcal{H}_1 j_n > a_n(t)e^{-iE_nt/\hbar} = \sum_n i\hbar \frac{d}{dt} a_n(t) j_n > e^{-iE_nt/\hbar}. \]

Forming inner products of both sides with an orthonormal state \(<m|\),
\[ <m| \sum_n \mathcal{H}_1 j_n > a_n(t)e^{-iE_nt/\hbar} = <m| \sum_n i\hbar \frac{d}{dt} a_n(t) j_n > e^{-iE_nt/\hbar} \]
\[ \sum_n <m| \mathcal{H}_1 j_n > a_n(t)e^{-iE_nt/\hbar} = \sum_n <m| i\hbar \frac{d}{dt} a_n(t) j_n > e^{-iE_nt/\hbar} \]
\[ = \sum_n i\hbar \frac{d}{dt} <m| j_n > e^{-iE_nt/\hbar}, \]

where \(<m|\) commutes with the derivative since it operates on the time dependent coefficient, and represents a number. This means
\[ \sum_n <m| \mathcal{H}_1 j_n > a_n(t)e^{-iE_nt/\hbar} = \sum_n i\hbar \frac{d}{dt} a_n(t) \delta_{m,n} e^{-iE_nt/\hbar} \]
\[ = i\hbar \frac{d}{dt} a_m(t) e^{-iE_m t/\hbar}, \]

where the summation is dropped because all terms where \(n \neq m\) are zero. Rearranging and combining the arguments of the exponentials, this is
\[ i\hbar \frac{d}{dt} a_m(t) = \sum_n <m| \mathcal{H}_1 j_n > a_n(t) e^{i(E_m - E_n) t/\hbar}. \]
Defining
\[ \omega_{m,n} = \frac{E_m - E_n}{\hbar}, \]
the last equation becomes
\[ i\hbar \frac{d}{dt} a_m(t) = \sum_n <m| \mathcal{H}_1 j_n > a_n(t) e^{i\omega_{m,n} t}. \]

Equation (18–4) is the result sought. It is, however, a coupled set of differential equations which we cannot solve in general. There are, nevertheless, a few important cases where equation (18–4) can be solved, and these have been exploited for as many as four Nobel prizes.

Example 18–1: Show equation (18–4) is a set of coupled differential equations.
Writing the first few terms of the summation explicitly demonstrates the tenet. For $n = 1$,

$$i\hbar \dot{a}_1(t) = <1 | \mathcal{H}_1 | 1> a_1(t) + <1 | \mathcal{H}_1 | 2> a_2(t)e^{i\omega_{12}t} + <1 | \mathcal{H}_1 | 3> a_3(t)e^{i\omega_{13}t} + \ldots.$$ 

For $n = 2$,

$$i\hbar \dot{a}_2(t) = <2 | \mathcal{H}_1 | 1> a_1(t)e^{i\omega_{21}t} + <2 | \mathcal{H}_1 | 2> a_2(t) + <2 | \mathcal{H}_1 | 3> a_3(t)e^{i\omega_{23}t} + \ldots.$$ 

The time derivative of $a_1(t)$ depends on $a_2(t)$, and the time derivative of $a_2(t)$ depends on $a_1(t)$. Thus, equation (18–4) is a set of coupled differential equations. Further, the time derivative of $a_1(t)$ depends on $a_3(t)$, and the time derivative of $a_3(t)$ depends on $a_1(t)$, and the time derivative of $a_2(t)$ depends on $a_3(t)$, and the time derivative of $a_3(t)$ depends on $a_2(t)$, and so on. In general, the first few terms of the summation are

$$i\hbar \dot{a}_m(t) = <m | \mathcal{H}_1 | 1> a_1(t)e^{i\omega_{m1}t} + <m | \mathcal{H}_1 | 2> a_2(t)e^{i\omega_{m2}t} + <m | \mathcal{H}_1 | 3> a_3(t)e^{i\omega_{m3}t} + \ldots,$$

so the coupling in general is infinite.

Equation (18–4) contains the notation of matrix elements, and by convention the braket portion of these matrix elements are commonly denoted

$$W_{ij} = <i | \mathcal{H}_1 | j>.$$  \hspace{1cm} (18–5)

**Example 18–2:** What is equation (18–4) in matrix form?

Drawing on example 18–1 and experience with matrices we hope you have developed at this point, the matrix form of equation (18–4) is

$$i\hbar \frac{d}{dt} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} = \begin{pmatrix} W_{11} & W_{12}e^{i\omega_{12}t} & W_{13}e^{i\omega_{13}t} \\ W_{21}e^{i\omega_{21}t} & W_{22} & W_{23}e^{i\omega_{23}t} \\ W_{31}e^{i\omega_{31}t} & W_{32}e^{i\omega_{32}t} & W_{33} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}.$$ 

**Two–Level Systems**

One special case of great importance and utility is based on the assumption there are only two levels in the system, a ground state and one excited state. This may appear unrealisitic initially, but real systems may be practically constrained such that only the ground state and one excited state are accessible. Four Nobel Prizes have been awarded for developments based on two–level systems. These are Rabi (1944) for work on molecular beams and nuclear magnetic resonance; Bloch and Purcell (1952) for research on nuclear magnetic moments; Townes, Basov, and Prochorov (1964) for quantum electronics leading to masers, lasers, and quantum optics; and Kastler (1966) for developing optical pumping. These four examples serve to illustrate the importance of the two–level system a wide variety of applications.

Again, the basis of the two level system is that there are but two accessible states, a ground state and one excited state, so equation (18–4) becomes

$$i\hbar \dot{a}_1(t) = <1 | \mathcal{H}_1 | 1> a_1(t) + <1 | \mathcal{H}_1 | 2> a_2(t)e^{i\omega_{12}t}$$

$$= W_{11}a_1(t) + W_{12}a_2(t)e^{i\omega_{12}t}.$$
and 

\[ i\hbar \dot{a}_2(t) = <2|H_1|1> a_1(t)e^{i\omega_{21}t} + <2|H_1|2> a_2(t) = W_{21}a_1(t)e^{i\omega_{21}t} + W_{22}a_2(t) \]

We expect \( H_0 \) is diagonal in some basis, where its eigenvalues are on the diagonal, and all off diagonal elements are zero. We expect a matrix representation of the complete Hamiltonian, \( H_0 + H_1 \) to have the eigenvalues of \( H_0 \) on the diagonal, but also non-zero off diagonal elements which describe the perturbation. If we subtract \( H_0 \) to get the matrix representation of just \( H_1 \), the diagonal elements will be zero and the only non-zero elements will be off diagonal elements. This is not absolutely necessary, a perturbation matrix can contain non-zero diagonal elements. Our discussion is much easier if diagonal elements of the perturbation matrix are zero, and generally this is the case. We assume diagonal elements of the perturbation matrix to be zero for the present, which means 

\[ W_{11} = W_{22} = 0 \]

where only the perturbation Hamiltonian is considered. The two-level specific equations from equation (18–4) then reduce to 

\[ i\hbar \dot{a}_1(t) = W_{12}a_2(t)e^{i\omega_{12}t}, \]

and 

\[ i\hbar \dot{a}_2(t) = W_{21}a_1(t)e^{i\omega_{21}t}. \]

Further, in a two-level system there are no other \( E_n \), so there is but one frequency of consequence with a positive and negative value, \( i.e., \omega_{21} = -\omega_{12} \). In accordance with convention we call this frequency \( \omega_0 \), \( i.e., \omega_0 \equiv \omega_{21} \). Then

\[ \dot{a}_1(t) = -\frac{i}{\hbar} W_{12}a_2(t)e^{-i\omega_{12}t}, \quad \text{and} \quad \dot{a}_2(t) = -\frac{i}{\hbar} W_{21}a_1(t)e^{i\omega_{21}t}. \] (18–6)

Equations (16–6) are exact, but not particularly useful because the \( a_n(t) \) are unknown. Subject to one additional assumption, these equations can be solved by a series of successive approximations.

**Example 18–3:** Show \( \omega_{21} = -\omega_{12} \).

Recalling the definition of equation (18–3),

\[ \omega_{21} = \frac{E_2 - E_1}{\hbar} = -\frac{E_1 - E_2}{\hbar} = -\omega_{12}. \]

The wave function will generally be a linear combination of the two states so equation (18–2) becomes

\[ |\psi(t)> = a_1(t)|1> e^{-iE_1t/\hbar} + a_2(t)|2> e^{-iE_2t/\hbar}. \]

The normalization condition requires

\[ |a_1(t)|^2 + |a_2(t)|^2 = 1. \]

**Example 18–4:** Show the normalization condition requires \( |a_1(t)|^2 + |a_2(t)|^2 = 1. \)

\[ 1 = <\psi(t)|\psi(t)> = (a_1^*(t)|1|e^{iE_1t/\hbar} + a_2^*(t)|2|e^{iE_2t/\hbar})(a_1(t)|1|e^{-iE_1t/\hbar} + a_2(t)|2|e^{-iE_2t/\hbar}) \]
\[ a_1^*(t) < 1 | e^{iE_1t/h} a_1(t) | 1 > e^{-iE_1t/h} + a_1^*(t) < 1 | e^{iE_1t/h} a_2(t) | 2 > e^{-iE_2t/h} \]
\[ + a_2^*(t) < 2 | e^{iE_2t/h} a_1(t) | 1 > e^{-iE_1t/h} + a_2^*(t) < 2 | e^{iE_2t/h} a_2(t) | 2 > e^{-iE_2t/h} \]
\[ = | a_1(t) |^2 < 1 | 1 > + a_1^*(t) a_2(t) < 1 \sqrt{2} | e^{i(E_1 - E_2)t/h} + a_2^*(t) a_1(t) < 2 \sqrt{2} | e^{i(E_2 - E_1)t/h} + | a_2(t) |^2 < 2 | 2 > , \]

where the inner product of unlike states is zero so those are struck. The inner product of like states is 1, so

\[ | a_1(t) |^2 + | a_2(t) |^2 = 1. \]

Equations (18–6) can be solved by a series of successive approximations using the additional assumption that the system originates in an eigenstate. We will pick the ground state. This means at time \( t = 0 \),
\[ a_1(0) = 1 \quad \text{and} \quad a_2(0) = 0, \]
so a “zeroth” order approximation is
\[ a_1^{(0)}(t) = 1 \quad \text{and} \quad a_2^{(0)}(t) = 0, \]

Using these in equations (18–6),
\[ \frac{da_1(t)}{dt} = 0 \quad \text{and} \quad \frac{da_2(t)}{dt} = -i \frac{\hbar}{W_21} W_21(t) e^{i\omega_0t}. \]

These are two variables separable differential equations which can be solved by integration to get first order approximations,
\[ a_2^{(1)}(t) = -i \frac{\hbar}{W_21} \int_0^t W_21(t') e^{i\omega_0t'} dt', \quad (18 - 7) \]

and
\[ a_1^{(1)}(t) = \text{constant} = 1 - | a_2(t) |^2 \approx 1, \quad (18 - 8) \]

assuming \( a_2^{(1)}(t) \ll 1 \).

**Example 18–5:** What are the second order approximations to \( a_1(t) \) and \( a_2(t) \)?

We can repeat the procedure to obtain the second-order corrections,
\[ \frac{da_2(t)}{dt} = -i \frac{\hbar}{W_21} W_21(t) e^{i\omega_0t} \quad \Rightarrow \quad a_2^{(2)}(t) = -i \frac{\hbar}{W_21} \int_0^t W_21(t') e^{i\omega_0t'} dt', \]

so the first and second order correction for the coefficient of the excited state are identical. The coefficient of the ground state is
\[ \frac{da_1(t)}{dt} = -i \frac{\hbar}{W_21} W_12(t) \left( -i \frac{\hbar}{W_21} \int_0^t W_21(t') e^{i\omega_0t'} dt' \right) e^{-i\omega_0t} \]
\[ = - \frac{1}{\hbar^2} W_12(t) e^{-i\omega_0t} \int_0^t W_21(t') e^{i\omega_0t'} dt' \]


\[ \Rightarrow a_1^{(2)}(t) = -\frac{1}{\hbar} \int_0^t W_{12}(t') e^{-i\omega_0 t'} \left( \int_0^{t'} W_{21}(t') e^{i\omega_0 t'} \, dt' \right) \, dt'', \]

where primes are used simply to clarify the variables of integration.

Though approximation can be made to arbitrary precision following the procedure illustrated in example 18–5, we will deal primarily with the first order approximations of equations (18–6).

**Example 18–6**: What is the first order coefficient of the excited state for a two level system for a small constant perturbation of finite duration?

Figure 18–1 illustrates a constant perturbation of finite duration. Using equation (18–7),

\[ a_2^{(1)}(t) = -\frac{i}{\hbar} \int_0^t W_{21}(t') e^{i\omega_0 t'} \, dt' \]

\[ = -\frac{i}{\hbar} W_{21} \int_0^t e^{i\omega_0 t'} \, dt' \]

where \( W_{21}(t') = W_{21} \) is a constant, so can be brought outside the integral. Then

\[ a_2^{(1)}(t) = -\frac{i}{\hbar} W_{21} \frac{1}{i\omega_0} e^{i\omega_0 t} \bigg|_0^t \]

\[ = -\frac{W_{21}}{\hbar \omega_0} (e^{i\omega_0 t} - 1). \]

**Example 18–7**: Calculate the probability for measuring the excited state of a two level system to a first order approximation for a small constant perturbation of finite duration.

We can calculate the indicated probability given the result of example 18–6, because probability is the square of the amplitude, \( i.e., \)

\[ P_2(t) = \left| a_2^{(1)}(t) \right|^2 \]

\[ = \left| -\frac{W_{21}}{\hbar \omega_0} (e^{i\omega_0 t} - 1) \right|^2 \]

\[ = \frac{W_{21}^2}{\hbar^2 \omega_0^2} (e^{-i\omega_0 t} - 1) (e^{i\omega_0 t} - 1) \]

\[ = \frac{W_{21}^2}{\hbar^2 \omega_0^2} (1 - e^{i\omega_0 t} - e^{-i\omega_0 t} + 1) \]

\[ = \frac{W_{21}^2}{\hbar^2 \omega_0^2} \left( 2 - \cos \omega_0 t - i \sin \omega_0 t - \cos \omega_0 t + i \sin \omega_0 t \right) \]

\[ = \frac{2W_{21}^2}{\hbar^2 \omega_0^2} (1 - \cos \omega_0 t) \]

\[ = \frac{2W_{21}^2}{\hbar^2 \omega_0^2} 2 \sin^2 \left( \frac{\omega_0 t}{2} \right) \]

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Figure 18–2 illustrates this probability function.

**Example 18–8:** What is the first order coefficient of the excited state for a two level system for the periodic perturbation $\mathcal{H}_1(t) = V_0(\vec{r}) \cos \omega t$?

The first order coefficient is

$$a_2^{(1)}(t) = -\frac{i}{\hbar} \int_0^t W_{21}(t') e^{i\omega_0 t'} dt'$$

where

$$W_{21}(t) = <2|\mathcal{H}_1(t)|1>$$

$$= <2|V_0(\vec{r}) \cos \omega t|1>$$

$$= <2|V_0(\vec{r})|1> \cos \omega t,$$

where $V_0(\vec{r})$ is not removed from the bra-ket because it is a function of spatial coordinates. The first order coefficient is

$$a_2^{(1)}(t) = -\frac{i}{\hbar} \int_0^t <2|V_0(\vec{r})|1> \cos \omega t' e^{i\omega_0 t'} dt'$$

$$= -\frac{i}{\hbar} <2|V_0(\vec{r})|1> \int_0^t \left( \frac{1}{2} e^{i\omega t'} + \frac{1}{2} e^{-i\omega t'} \right) e^{i\omega_0 t'} dt'$$

$$= -\frac{i}{2\hbar} <2|V_0(\vec{r})|1> \left( \frac{e^{i(\omega_0+\omega)t'} - \frac{1}{\omega_0+\omega} e^{i(\omega_0-\omega)t'}}{i(\omega_0-\omega)} + \frac{e^{i(\omega_0-\omega)t'} - \frac{1}{\omega_0-\omega} e^{i(\omega_0+\omega)t'}}{i(\omega_0+\omega)} \right).$$

**Example 18–9:** Evaluate the first order coefficient of the excited state for a two level system for the periodic perturbation $\mathcal{H}_1(t) = V_0(\vec{r}) \cos \omega t$ at resonance.

Resonance means $\omega \approx \omega_0$. If $\omega \approx \omega_0$, the second term dominates the first, or

$$a_2^{(1)}(t) \approx -\frac{1}{2\hbar} <2|V_0(\vec{r})|1> \frac{e^{i(\omega_0-\omega)t'} - \frac{1}{\omega_0-\omega} e^{i(\omega_0+\omega)t'}}{(\omega_0-\omega)}.$$

**Example 18–10:** Calculate the probability for measuring the excited state of a two level system to a first order approximation for a small periodic perturbation.
The only significant contribution to this probability will be when \( \omega \approx \omega_0 \), so

\[
P_2(t) = \left| a_2^{(1)}(t) \right|^2
\]

\[
\approx \left( -\frac{1}{2\hbar} \langle \overrightarrow{r} | V_0(\overrightarrow{r}) | 1 \rangle^* \frac{e^{-i(\omega_0 - \omega)t'} - 1}{(\omega_0 - \omega)} \right) \left( -\frac{1}{2\hbar} \langle \overrightarrow{r} | V_0(\overrightarrow{r}) | 1 \rangle \frac{e^{i(\omega_0 - \omega)t'} - 1}{(\omega_0 - \omega)} \right)
\]

\[
= \frac{1}{4\hbar^2} \left| \langle \overrightarrow{r} | V_0(\overrightarrow{r}) | 1 \rangle \right|^2 \left( \frac{2(1 - \cos(\omega_0 - \omega)t)}{(\omega_0 - \omega)^2} \right)
\]

\[
= \frac{1}{2\hbar^2} \left| W_{21} \right|^2 \left( \frac{2 \sin^2 \left( \frac{(\omega_0 - \omega)t}{2} \right)}{(\omega_0 - \omega)^2} \right)
\]

\[
= \frac{1}{\hbar^2} \left| W_{21} \right|^2 \left( \frac{\sin^2 \left( \frac{(\omega_0 - \omega)t}{2} \right)}{(\omega_0 - \omega)^2} \right)
\]

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**Figure 18–3.** The probability curve for a two level system.

Figure 18–3 illustrates the probability curve for a two level system. Notice that it is sharply peaked around the resonant frequency.

**Multi–Level Systems**

Equation (18–4),

\[
i\hbar \frac{d a_m(t)}{dt} = \sum_n <m | \mathcal{H}_1 | n> a_n(t) e^{i\omega_{mn}t},
\]

is exact. This set of coupled differential equations is equivalent to the Schrodinger equation. Two–level systems are convenient because the summation is short. However, even in “real two–level systems” there are actually an infinite number of eigenstates; we make all but two states inaccessible to obtain a practical two–level system. We return to equation (18–4) to address systems where more than two states are accessible. Remember we are treating a system with a time dependent Hamiltonian \( \mathcal{H}(t) \) as a sum of a time independent Hamiltonian and a small pertubation Hamiltonian, \( \mathcal{H}(t) = \mathcal{H}_0 + \mathcal{H}_1(t) \). We can express the same idea using

\[
\mathcal{H}(t) = \mathcal{H}_0 + \lambda \mathcal{H}_1(t), \quad (18–9)
\]
where the factor $\lambda$ is a parameter which can be varied to meter the amount of the perturbation. If $\lambda = 1$, equation (18–9) reduces to $\mathcal{H}(t) = \mathcal{H}_0 + \mathcal{H}_1(t)$, as before. The parameter $\lambda$ does not actually appear in the solution we seek, so can be any constant, though the development is likely most approachable if you picture $\lambda$ to be one or less. Were we to use equation (18–9) to develop equation (18–4), we would obtain

$$i\hbar \frac{d a_m(t)}{dt} = \sum_{j} \langle m | \lambda \mathcal{H}_1 | j \rangle a_j(t) e^{i\omega_{mj}t},$$

$$= \sum_{j} \langle m | \mathcal{H}_1 | j \rangle \lambda a_j(t) e^{i\omega_{mj}t}. \quad (18 - 10)$$

We can also expand the coefficient $a_n(t)$ in a power series in the parameter $\lambda$, meaning

$$a_n(t) = a_n^{(0)}(t) + \lambda a_n^{(1)}(t) + \lambda^2 a_n^{(2)}(t) + \lambda^3 a_n^{(3)}(t) + \cdots,$$

where the order of the correction is indicated by the superscript. Using this expansion in equation (18–10),

$$i\hbar \frac{d}{dt} (a_n^{(0)}(t) + \lambda a_n^{(1)}(t) + \lambda^2 a_n^{(2)}(t) + \cdots) = \sum_{j} \langle m | \mathcal{H}_1 | j \rangle \lambda (a_j^{(0)}(t) + \lambda a_j^{(1)}(t) + \lambda^2 a_j^{(2)}(t) + \cdots) e^{i\omega_{mj}t}$$

$$= \sum_{j} \langle m | \mathcal{H}_1 | j \rangle (\lambda a_j^{(0)}(t) + \lambda^2 a_j^{(1)}(t) + \lambda^3 a_j^{(2)}(t) + \cdots) e^{i\omega_{mj}t}.$$  

The mysterious reason to use the parameter $\lambda$ is that the last equation must be true term by term for similar powers of $\lambda$, i.e.,

$$i\hbar \frac{d}{dt} \lambda^k a_m^{(k)}(t) = \sum_{j} \langle m | \mathcal{H}_1 | j \rangle \lambda^k a_j^{(k-1)}(t) e^{i\omega_{mj}t}$$

$$\Rightarrow i\hbar \frac{d}{dt} a_m^{(k)}(t) = \sum_{j} \langle m | \mathcal{H}_1 | j \rangle a_j^{(k-1)}(t) e^{i\omega_{mj}t},$$

where the factor $\lambda^k$ is canceled from both sides. Most importantly,

$$i\hbar \frac{d}{dt} a_m^{(1)}(t) = \sum_{j} \langle m | \mathcal{H}_1 | j \rangle a_j^{(0)}(t) e^{i\omega_{mj}t},$$

$$\Rightarrow a_m^{(1)}(t) = -\frac{i}{\hbar} \int_0^t \sum_{j} \langle m | \mathcal{H}_1 | j \rangle a_j^{(0)}(t') e^{i\omega_{mj}t'} dt'.$$

(18 – 11)

Similar to the two–level system, if the system originates in an eigenstate, say the eigenstate $n$, $a_j^{(0)}(0) = 0$, and for the system in which the system originates, $a_j^{(0)}(0) = 1$, because we assume the system is normalized. In other words,

$$a_j^{(0)}(0) = \delta_{j,n}.$$
for a system in the \( j \)th eigenstate at time \( t = 0 \). The summation is then one term, so equation (18–11) becomes

\[
a_m^{(1)}(t) = -\frac{i}{\hbar} \int_0^t <m|\mathcal{H}_1|n> e^{i\omega_{mn}t'} dt',
\]

where the coefficient is excluded because \( a_n^{(0)}(t') \approx 1 \) if the perturbation is small. Using the notation

\[
W_{mn} = <m|\mathcal{H}_1|n>,
\]

the last equation becomes

\[
a_m^{(1)}(t) = -\frac{i}{\hbar} \int_0^t W_{mn}(t')e^{i\omega_{mn}t'} dt',
\]

(18 – 12)

which is the result we seek. This is the first order correction to the \( m \)th coefficient. If higher order corrections are small,

\[
a_m(t) \approx a_n^{(0)}(t) + a_m^{(1)}(t) = a_m^{(1)}(t).
\]

Because of this fact, the superscripts are often simply excluded.

The quantity \( |a_m^{(1)}(t)|^2 \) is the probability of finding the system in state \( m \) at time \( t \). If the system started in the \( j \)th state, \( |a_m^{(1)}(t)|^2 \) is the probability a transition from state \( n \) to state \( m \) will have occurred during time \( t \).

Notice the similarity between equations (18–12) and (18–7). Except for the indices, they are identical.

**Example 18–11:** Assume a multi–level system is in an eigenstate. Find the probability of measuring the \( m \)th excited state at time \( t \) if the system is disturbed by a small constant perturbation of duration \( t \).

The math is the same as examples 18–6 and 18–7, so we will simply give the results in multi–state notation. The coefficient of the \( m \)th state is

\[
a_m^{(1)}(t) = -\frac{W_{mn}}{\hbar\omega_{mn}} (e^{i\omega_{mn}t} - 1),
\]

following the development of example (18–6). The index \( n \) denotes the original eigenstate. Here

\[
W_{mn} = <m|V_0|n>, \quad \text{and} \quad \hbar\omega_{mn} = E_m - E_n.
\]

The probability is the square of this coefficient,

\[
P_m(t) = |a_m^{(1)}(t)|^2 = \frac{4W_{mn}^2}{\hbar^2\omega_{mn}^2} \sin^2 \left( \frac{\omega_{mn}t}{2} \right)
\]

following the development of example 18–7.

**Example 18–12:** For a multi–level system, find the probability of a transition to the \( m \)th state for a periodic perturbation near the resonant frequency.
A periodic perturbation would be of the form $H_1(t) = V_0(\vec{r}) \cos \omega t$. The coefficient of the $m$th state is

$$a_m^{(1)}(t) = -\frac{1}{2\hbar} <m | V_0(\vec{r}) | n> \left( e^{i(\omega mn + \omega) t'} - 1 + e^{i(\omega mn - \omega) t'} - 1 \right).$$

Near the resonant frequency,

$$a_m^{(1)}(t) \approx -\frac{1}{2\hbar} <m | V_0(\vec{r}) | n> \frac{e^{i(\omega mn - \omega) t'} - 1}{(\omega mn - \omega)}.$$

The probability is

$$P_m(t) = \frac{|a_m^{(1)}(t)|^2}{\hbar^2} |W_{mn}|^2 \left( \frac{\sin^2 \left( \frac{(\omega mn - \omega) t}{2} \right)}{(\omega mn - \omega)^2} \right).$$

The mathematical development follows that seen in examples 18–8 through 18–10.

**Example 18–13:** A multi–level system is exposed to the electric field $\vec{E} = E_0 \cos(\omega t) \hat{k}$. What is the probability of a transition from the $n$th eigenstate to the $m$th eigenstate as a function of time?

The perturbation is described by $\mathcal{H}_1 = -q \Phi(\vec{r})$. Elementary electromagnetics tells us

$$E = -\frac{d \Phi(\vec{r})}{dr} = -\frac{d \Phi(\vec{r})}{dz}$$

for a field oriented in the $\hat{k}$ direction. Then

$$d \Phi(\vec{r}) = -E dz = E_0 \cos(\omega t) dz$$

$$\Rightarrow \Phi(\vec{r}) = -\int E_0 \cos(\omega t) dz = -E_0 \cos(\omega t) \int dz = -E_0 z \cos(\omega t),$$

so the perturbation in terms of the periodic electric field is

$$\mathcal{H}_1(t) = E_0 q z \cos(\omega t),$$

and what we have is an application of the last example where $V_0 \rightarrow E_0 q z$. Using this in the result of example 18–12,

$$P_m(t) = \frac{1}{\hbar^2} |<m | E_0 q z | n>|^2 \left( \frac{\sin^2 \left( \frac{(\omega mn - \omega) t}{2} \right)}{(\omega mn - \omega)^2} \right)^2$$

$$= \frac{E_0^2 q^2}{\hbar^2} |<m | z | n>|^2 \left( \frac{\sin^2 \left( \frac{(\omega mn - \omega) t}{2} \right)}{(\omega mn - \omega)^2} \right).$$
## Transition Rates

Generally, transition rate is the time rate of change of probability,

\[ R \equiv \frac{dP(t)}{dt}, \quad (18 - 13) \]

however, in a multi-level system, there is an additional consideration. Notice that figure 18–3, for instance, is sharply spiked, but it is not a delta function. We could only use equation (18–13) for a two level system, or we could say that equation (18–13) is the transition rate per state. We are interested in the probability

\[ \sum |a_m(t)|^2 \]

vice just \[ |a_m(t)|^2 \]. One convention is to use a density of states \[ \rho(\omega) \], which is a number per unit frequency interval \[ \omega \]. Assuming the states are spaced closely enough to approximate a continuum,

\[ P(t) = \sum |a_m(t)|^2 \rightarrow \int_{-\infty}^{\infty} |a_m(t)|^2 \rho(\omega) d\omega. \]

Now equation (18–13) applies, i.e.,

\[ R_{n \rightarrow m} = \frac{d}{dt} \int_{-\infty}^{\infty} |a_m(t)|^2 \rho(\omega) d\omega, \]

and since the definite integral is an unevaluated number, this can be treated as a variable separable differential equation, or

\[ R_{n \rightarrow m} dt = d \left( \int_{-\infty}^{\infty} |a_m(t)|^2 \rho(\omega) d\omega \right) \]

\[ \Rightarrow R_{n \rightarrow m} = \frac{1}{t} \int_{-\infty}^{\infty} |a_m(t)|^2 \rho(\omega) d\omega. \]

The last equation is used often assuming \[ \rho(\omega) \] varies slowly over the range of interest, so is treated as a constant. Treating the density of states as a constant, the transition rate described in example 18–13 is

\[ R_{i \rightarrow f} = \frac{\rho(\omega_{if})}{t} \int_{-\infty}^{\infty} |a_f(t)|^2 d\omega, \quad (18 - 14) \]

where \( i \) and \( f \) stand for initial and final states respectively.

### Example 18–14:

What is the transition rate for the multi-level system exposed to the electric field \( \vec{E} = E_0 \cos(\omega t) \hat{k} \)?

Using equation (18–14),

\[ R_{i \rightarrow f} = \frac{\rho(\omega_{if})}{t} \int_{-\infty}^{\infty} \frac{E_0^2 q^2}{h^2} |f \rangle \langle z| \langle i| \langle f | \langle z| \langle i| \equiv 2 \left( \frac{\sin^2 \left( \frac{(\omega_{if} - \omega) t}{2} \right)}{(\omega_{if} - \omega)^2} \right) d\omega \]

\[ = \frac{E_0^2 q^2}{h^2} |f \rangle \langle z| \langle i| \langle f | \langle z| \langle i| \equiv 2 \frac{\rho(\omega_{if})}{t} \int_{-\infty}^{\infty} \left( \frac{\sin^2 \left( \frac{(\omega_{if} - \omega) t}{2} \right)}{(\omega_{if} - \omega)^2} \right) d\omega. \]

Changing variables to do the integration, where

\[ \frac{(\omega - \omega_{fi})}{2} t = x \quad \Rightarrow \quad \omega_{fi} - \omega = -\frac{2}{t} x \]
\[ d\omega = \frac{2}{t} \, dx \quad \text{and} \quad (\omega_{fi} - \omega)^2 = \frac{4}{t^2} x^2, \]

and notice the sign of the differential is not particularly pertinent, because it only indicates an increase or decrease in energy, so

\[
R_{i-f} = \frac{E_0^2 q^2}{\hbar^2} \left| f \right| z \left| i \right> \frac{2 \rho(\omega_{if})}{t} \int_{-\infty}^{\infty} \frac{\sin^2(x)}{x^2} \, \frac{2}{t} \, dx
\]

\[ = \frac{E_0^2 q^2}{2\hbar^2} \left| f \right| z \left| i \right> \frac{2 \rho(\omega_{if})}{t} \int_{-\infty}^{\infty} \frac{\sin^2(x)}{x^2} \, dx\]

and since

\[ \int_{-\infty}^{\infty} \frac{\sin^2(x)}{x^2} \, dx = \pi, \]

\[
R_{i-f} = \frac{E_0^2 q^2 \pi}{2\hbar^2} \left| f \right| z \left| i \right> \frac{2 \rho(\omega_{if})}{t}.
\]