CHM 502 – Module 6 – Time-Dependent Perturbation Theory & Light-Matter Interactions

Prof. Marissa Weichman

We have now considered the effects of small, time-independent perturbations to various quantum systems. But what happens when we subject an atom or molecule to a time-*dependent* perturbation, e.g. the oscillating electromagnetic field of a laser beam?

In time-independent perturbation theory we asked "what are the new eigenstates and eigenenergies of the perturbed system?" In time-dependent perturbation theory (TDPT), it's not as helpful to ask about the eigenstates and eigenenergies of a system with a time-varying Hamiltonian. Instead, we phrase our driving question as "What is the probability that the system has undergone a transition from an initial state i (of the time-independent reference Hamiltonian) to a final state f (of the time-independent reference Hamiltonian) some time t after a perturbation is applied?"

1 Laying out the problem

The problem we will consider has the total Hamiltonian:

$$\hat{H}(t) = \hat{H}^{(0)} + \lambda \hat{H}^{(1)}(t) \tag{1}$$

where again λ is a label for bookkeeping.

We assume our zeroth-order reference Hamiltonian $\hat{H}^{(0)}$ is time-independent and has energy eigenstates $|\psi_n\rangle$ that obey the time-independent Schrödinger equation:

$$\hat{H}^{(0)} |\psi_n\rangle = E_n |\psi_n\rangle \equiv \hbar\omega_n |\psi_n\rangle \tag{2}$$

Suppose that at time $t = 0$, the system is initialized in an eigenstate of $\hat{H}^{(0)}$, with $|\Psi(0)\rangle = |\psi_i\rangle$. At some later time t following evolution under $\hat{H}(t)$, the system can be found in state $|\Psi(t)\rangle$. We expand $|\Psi(t)\rangle$ in terms of our $|\psi_n\rangle$ basis:

$$|\Psi(t)\rangle = \sum_n c_n(t) |\psi_n\rangle \tag{3}$$

with initial conditions given by $c_n(0) = \delta_{ni}$. The probability that the system is in state $|\psi_f\rangle$ at time t is simply $|c_f(t)|^2$. Therefore, our goal is to find

$$P_{f \leftarrow i}(t) = |c_f(t)|^2 \tag{4}$$

which is the probability that the $\hat{H}^{(1)}(t)$ perturbation has induced a transition from initial state $|\psi_i\rangle$ to final state $|\psi_f\rangle$ when we check in with our system at time t.

To attack this problem, we will proceed as follows:

- substitute our expansion for $|\Psi(t)\rangle$ into the time-*dependent* Schrödinger equation
- left-project with $\langle\psi_f|$
- expand $c_n(t)$ as a Taylor series in λ
- separate orders of λ and see what we can learn

2 The first-order solutions

Let's begin with the time-dependent Schrödinger equation. Our total wavefunction must obey:

$$i\hbar\,|\dot{\Psi}(t)\rangle = \hat{H}(t)\;|\Psi(t)\rangle = \left[\hat{H}^{(0)} + \lambda\hat{H}^{(1)}(t)\right]|\Psi(t)\rangle \tag{5}$$

Now, we left project with $\langle\psi_f|$ and substitute in our expansion for $|\Psi(t)\rangle$ from Eqn. 2:

$$i\hbar\,\langle\psi_f|\sum_n \dot{c}_n(t)\,|\psi_n\rangle = \langle\psi_f|\left[\hat{H}^{(0)} + \lambda\hat{H}^{(1)}(t)\right]\sum_n c_n(t)\,|\psi_n\rangle \tag{6}$$

$$= i\hbar\sum_n \dot{c}_n(t)\delta_{fn} = \sum_n c_n(t)\,\langle\psi_f|\hat{H}^{(0)}|\psi_n\rangle + \lambda\sum_n c_n(t)\,\langle\psi_f|\hat{H}^{(1)}(t)|\psi_n\rangle \tag{7}$$

$$= i\hbar\dot{c}_f(t) = \sum_n c_n(t)\cdot E_n\cdot\delta_{fn} + \lambda\sum_n c_n(t)\cdot H^{(1)}_{fn}(t) \tag{8}$$

$$\rightarrow \quad i\hbar\dot{c}_f(t) = E_f\cdot c_f(t) + \lambda\sum_n c_n(t)\cdot H^{(1)}_{fn}(t) \tag{9}$$

If we remove the perturbation for a moment by setting $\lambda = 0$, we find that:

$$i\hbar\dot{c}^{(0)}_f(t) = E_f\cdot c_f(t) \tag{10}$$

$$\rightarrow c^{(0)}_f(t) = c\cdot e^{-iE_ft/\hbar} \equiv c\cdot e^{-i\omega_f t} \tag{11}$$

This is exactly the complex sinusoidal time-dependence we expect for a stationary state of the time-independent reference Hamiltonian.

When we take $\lambda \neq 0$, $c_f(t)$ will feature both complex sinusoidal oscillations as well as more interesting dynamics due to the perturbation. To make things simpler, let's define:

$$c_f(t) = e^{-iE_ft/\hbar}\cdot b_f(t) \tag{12}$$

Here, $b_f(t)$ contains only the "interesting" time-dependence that we get after factoring out the phase behavior of our unperturbed stationary-states. (Note: this is essentially the same idea as working in the interaction picture, which we discussed back in Module 2.)

Armed with this definition of $b_f(t)$, let's plug Eqn. 12 into Eqn. 9:

$$i\hbar\dot{c}_f(t) = i\hbar\left[\dot{b}_f(t)\cdot e^{-i\omega_f t} + \cancel{b_f(t)\cdot e^{-i\omega_f t}\cdot(-i\omega_f)}\right] \qquad \text{LHS} \tag{13}$$

$$= \cancel{E_f\cdot b_f(t)\cdot e^{-i\omega_f t}} + \lambda\sum_n b_n(t)\cdot e^{-i\omega_n t}\,H^{(1)}_{fn}(t) \qquad \text{RHS} \tag{14}$$

$$\rightarrow \quad \boxed{i\hbar\dot{b}_f(t) = \lambda\sum_n b_n(t)\;H^{(1)}_{fn}(t)\;e^{i(\omega_f-\omega_n)t}} \tag{15}$$

Up to this point we have made no approximations, and Eqn. 15 is exact. The difficulty in solving Eqn. 15 arises from the fact that each $b_n(t)$ coefficient is defined in terms of all the others.

We will move forward by **(a)** assuming the perturbation is sufficiently weak that we can Taylor expand the $b_f(t)$ coefficients, keeping only the terms that are first-order in λ and **(b)** choosing a simple initial condition with our system prepared in state $|\psi_i\rangle$ at $t = 0$.

We begin by expanding $b_f(t)$ in powers of λ:

$$b_f(t) = b^{(0)}_f + \lambda b^{(1)}_f(t) + \cdots \tag{16}$$

Here, $b^{(0)}_f$ is time-independent, because all zeroth-order time dependence is captured by the complex exponential in Eqn. 12.

Now substituting this expansion of $b_f(t)$ into Eqn. 15:

$$i\hbar\frac{d}{dt}\left[b^{(0)}_f + \lambda b^{(1)}_f(t) + \cdots\right] = \lambda\sum_n\left[b^{(0)}_n + \lambda b^{(1)}_n(t) + \cdots\right]H^{(1)}_{fn}(t)\;e^{i(\omega_f-\omega_n)t} \tag{17}$$

Grouping just the terms that are first order in λ, we find:

$$i\hbar\dot{b}^{(1)}_f(t) = \sum_n b^{(0)}_n(t)\;H^{(1)}_{fn}\;e^{i(\omega_f-\omega_n)t} \tag{18}$$

Now we assume that our system is initialized in the i^{th} eigenstate of the reference Hamiltonian so $b^{(0)}_n = \delta_{ni}$. We therefore find:

$$i\hbar\dot{b}^{(1)}_f(t) = H^{(1)}_{fi}(t)\;e^{i(\omega_f-\omega_i)t} = \langle\psi_f|\hat{H}^{(1)}(t)|\psi_i\rangle\;\;e^{i\omega_{fi}t} \tag{19}$$

where $\omega_{fi} \equiv \omega_f - \omega_i$.

Now to solve for $b^{(1)}_f(t)$, we simply integrate in time:

$$b^{(1)}_f(t) - \cancel{b^{(1)}_f(0)}^{\,0} = \frac{1}{i\hbar}\int_0^t dt'\;\langle\psi_f|\hat{H}^{(1)}(t')|\psi_i\rangle\;\;e^{i\omega_{fi}t'} \tag{20}$$

And we can finally return to our initial desired quantity:

$$P_{f\leftarrow i}(t) = \left|c_f(t)\right|^2 = \left|e^{-i\omega_f t}\right|^2\cdot\left|\cancel{b^{(0)}_f}^{\,0} + \lambda b^{(1)}_f(t) + \cdots\right|^2 \approx \lambda^2\,|b^{(1)}_f(t)|^2 \tag{21}$$

where $b^{(1)}_f(t)$ is obtained using Eqn. 20 for a given perturbation $\hat{H}^{(1)}(t)$.

Note that as of Eqn. 16 we have forced the $c_f(t)$ coefficients to demonstrate only small first-order changes from their initial values. We pay a price for this! Our result in Eqn. 20 holds only for perturbations that are sufficiently weak that they don't significantly alter the state of the system.

3 An adiabatic time-dependent perturbation

One simple example that we can treat with TDPT is a perturbation that is switched on very slowly:

$$\hat{H}(t) = \hat{H}_0 + \hat{H}^{(1)}(t) \tag{22}$$

$$\hat{H}^{(1)}(t) = \begin{cases} 0 & t \leq 0 \\ \hat{V}(1 - e^{-kt}) & t > 0 \end{cases} \tag{23}$$

Note that this Hamiltonian reaches a time-independent form in the long-time limit:

$$\hat{H}(t \gg 1/k) = \hat{H}_0 + \hat{V} \tag{24}$$

We initialize the system in the $|\psi_i\rangle$ eigenstate of $\hat{H}_0$ and want to find the probability of ending up in $|\psi_f\rangle$ at time t. We find the time-dependent expansion coefficients of the wavefunction using Eqn. 20:

$$b_f^{(1)}(t) = \frac{1}{i\hbar} \int_0^t dt' \ \langle \psi_f | \hat{V}(1 - e^{-kt'}) | \psi_i \rangle \ e^{i\omega_{fi} t'} \tag{25}$$

$$= \frac{1}{i\hbar} \langle \psi_f | \hat{V} | \psi_i \rangle \int_0^t dt' \, (1 - e^{-kt'}) e^{i\omega_{fi} t'} \tag{26}$$

$$= \frac{V_{fi}}{i\hbar} \int_0^t dt' \ \left[e^{i\omega_{fi} t'} - e^{(i\omega_{fi} - k)t'} \right] \tag{27}$$

$$= \frac{V_{fi}}{i\hbar} \left[\frac{1}{i\omega_{fi}} \left[e^{i\omega_{fi} t} - 1 \right] - \frac{1}{i\omega_{fi} - k} \left[e^{i\omega_{fi} t} e^{-kt} - 1 \right] \right] \tag{28}$$

We will consider the case for a process that turns on *slowly* ($k \ll \omega_{if}$) in the *long-time* ($t \gg 1/k$) limit. Applying these limits, the above expression simplifies to:

$$b_f^{(1)}(t) = \frac{V_{fi}}{i\hbar} \left[\frac{1}{i\omega_{fi}} \left[e^{i\omega_{fi} t} - 1 \right] - \frac{1}{i\omega_{fi}} \left[-1 \right] \right] \tag{29}$$

$$= -\frac{V_{fi} \cdot e^{i\omega_{fi} t}}{\hbar \omega_{fi}} = -\frac{V_{fi} \cdot e^{i\omega_{fi} t}}{E_f - E_i} = \frac{V_{fi} \cdot e^{i\omega_{fi} t}}{E_i - E_f} \tag{30}$$

$$\rightarrow \quad P_{f \leftarrow i} = \left| b_f^{(1)}(t) \right|^2 = \frac{|V_{fi}|^2}{[E_f - E_i]^2} \tag{31}$$

Eqn. 30 should look familiar: it is nearly identical to the expansion coefficients of the i^{th} first-order wavefunction in time-*independent* perturbation theory, where we found

$$c_{fi}^{(1)} = \frac{H_{fi}^{(1)}}{E_i^{(0)} - E_f^{(0)}} \tag{32}$$

Where now $\hat{V}$ is standing in for $\hat{H}^{(1)}$.

What is happening here? When we turn on the perturbation slowly enough, the system adiabatically finds its way to the stationary states of the final Hamiltonian, which is given here by

$\hat{H}(t \to \infty) = \hat{H}_0 + \hat{V}$. Since we have taken the limit where this process happens adiabatically, the system *remains in the i^{th} energy level at any given moment* throughout the whole process.

This result is a statement of the quantum adiabatic theorem: provided the Hamiltonian changes slowly enough, if the system is initialized in the i^{th} eigenstate of the initial Hamiltonian it will end up in the corresponding i^{th} eigenstate of the final Hamiltonian.

4 A weak sinusoidal perturbation

Let's now turn our attention to light-matter interactions. Consider a molecule with permanent dipole moment $\underline{\hat{\mu}}$. Note that the dipole moment is both a vector in 3D space (indicated here by the single underline) and a quantum operator corresponding to the dipole moment observable:

$$\underline{\hat{\mu}} = \sum_n q_n \cdot \underline{r_n} \tag{33}$$

which describes the spatial distribution of charges (e.g. nuclei, electrons) in the molecule.

The molecule is interacting with perfectly monochromatic radiation, e.g. from a precise continuous wave (cw) laser light source. The oscillating electric field of the light is given by

$$\underline{E}(t) = \underline{\xi} \cos \omega t \tag{34}$$

Where $\underline{\xi}$ describes both the amplitude and the polarization of the electric field. This field will turn on at time $t = 0$ and persist until time t. Again, our question is: for a molecule initialized in an eigenstate $|\psi_i\rangle$ of $\hat{H}_0$ at $t = 0$, what is the probability that we will find it in eigenstate $|\psi_f\rangle$ when the field is switched off at time t?

We can write the time-dependent perturbation to our Hamiltonian as:

$$\hat{H}^{(1)}(t) = \underline{\hat{\mu}} \cdot \underline{E}(t) = \underline{\hat{\mu}} \cdot \underline{\xi} \cos \omega t \equiv \frac{\hat{V}}{2} \left[e^{i\omega t} + e^{-i\omega t} \right] \tag{35}$$

where we have defined $\hat{V} \equiv \underline{\hat{\mu}} \cdot \underline{\xi}$ for compactness.

We now calculate the probability that the system is found in state f at time t:

$$b_f^{(1)}(t) = \frac{1}{i\hbar} \int_0^t dt' \ \langle \psi_f | \frac{\hat{V}}{2} \left[e^{i\omega t'} + e^{-i\omega t'} \right] | \psi_i \rangle \ e^{i\omega_{fi} t'} \tag{36}$$

$$= \frac{V_{fi}}{2i\hbar} \int_0^t dt' \left[e^{i\omega t'} + e^{-i\omega t'} \right] e^{i\omega_{fi} t'} \tag{37}$$

$$= \frac{V_{fi}}{2i\hbar} \int_0^t dt' \left[e^{i(\omega_{fi} + \omega) t'} + e^{i(\omega_{fi} - \omega) t'} \right] \tag{38}$$

$$= \frac{V_{fi}}{2\hbar} \left[\frac{1 - e^{i(\omega_{fi} + \omega)t}}{(\omega_{fi} + \omega)} + \frac{1 - e^{i(\omega_{fi} - \omega)t}}{(\omega_{fi} - \omega)} \right] \tag{39}$$

Inspecting our result, let's note a few things:

(i) $b_f^{(1)}(t)$ depends on $V_{fi} \propto \langle \psi_f | \underline{\hat{\mu}} | \psi_i \rangle$. This dependence leads to dipole-allowed spectroscopic selection rules. Much more on this to come.

(ii) $b_f^{(1)}(t)$ depends on the frequency of the light ω. This leads to the prospect of resonant behavior: as $\omega \to \pm\omega_{fi}$ we will observe absorption or stimulated emission of light. (Note: spontaneous emission does not arise naturally out of first-order PT; more on this to come, too.)

Let's now consider resonant excitation, where $\omega \approx \omega_{fi}$. In this limit, the second term of Eqn. 39 dominates as its denominator approaches zero, so we drop the first term entirely. We find:

$$P_{f\leftarrow i}(t) = \left|b_f^{(1)}(t)\right|^2 = \frac{|V_{fi}|^2}{4\hbar^2}\left|\frac{1-e^{i(\omega_{fi}-\omega)t}}{\omega_{fi}-\omega}\right|^2 \tag{40}$$

$$= \frac{|V_{fi}|^2}{4\hbar^2(\omega_{fi}-\omega)^2}\left[1-e^{i(\omega_{fi}-\omega)t}\right]\left[1-e^{-i(\omega_{fi}-\omega)t}\right] \tag{41}$$

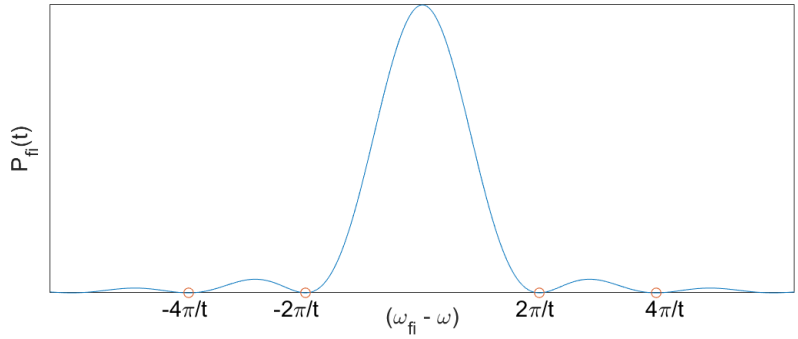
$$= \frac{|V_{fi}|^2}{4\hbar^2(\omega_{fi}-\omega)^2}\left[1-e^{i(\omega_{fi}-\omega)t}-e^{-i(\omega_{fi}-\omega)t}+1\right] \tag{42}$$

$$= \frac{|V_{fi}|^2}{4\hbar^2(\omega_{fi}-\omega)^2}\left[2-2\cos\left[(\omega_{fi}-\omega)t\right]\right] \tag{43}$$

$$= \frac{|V_{fi}|^2}{4\hbar^2}\cdot\frac{4\sin^2[\frac{1}{2}(\omega_{fi}-\omega)t]}{(\omega_{fi}-\omega)^2} = \frac{|V_{fi}|^2}{4\hbar^2}\cdot\left[\frac{\sin[\frac{1}{2}(\omega_{fi}-\omega)t]}{\frac{1}{2}(\omega_{fi}-\omega)}\right]^2 \tag{44}$$

where in the last step we used the trigonometric identity $2\sin^2\theta = 1-\cos 2\theta$.

This probability distribution takes the form of the square of a "sinc" function in frequency where $\mathrm{sinc}(x) \equiv \sin(x)/x$.



Let's use this distribution to make some observations:

(a) **What does the transition lineshape look like in frequency space?**

As a sinc function in frequency, $P_{f\leftarrow i} = 0$ when

$$\omega_{fi} - \omega = \pm\, 2n\pi/t \qquad \text{for} \qquad n = 1, 2, \ldots \tag{45}$$

The zeros closest to the resonance occur at $\omega = \omega_{fi} \pm 2\pi/t$. The central resonance therefore has an approximate linewidth of $4\pi/t$.

Therefore, the longer the interaction time with monochromatic radiation t, the narrower the central resonance appears in frequency space. This is a property of Fourier transforms: the longer the period of time that you have to observe an oscillation, the more accurately you can determine the precise frequency of that oscillation.

This phenomenon is sometimes referred to as the time-energy uncertainty relation. In our present case, we might handwave something like:

$$\Delta E = \hbar \Delta\omega \simeq \hbar \, \frac{4\pi}{\Delta t} \qquad \rightarrow \qquad \Delta E \Delta t \simeq 4\pi\hbar \tag{46}$$

This is not a true uncertainty relation like $\Delta x \Delta p \geq \hbar/2$, since time is not an operator.

Finally, remember that everything we have derived here assumes a perfect continuous wave field and ignores any homogeneous or heterogeneous broadening of the molecular transitions (more on that later). The sinc^2 lineshape we see here arises only from the limited interaction time of the molecule in the field.

(b) **What is the probability of making the $i \rightarrow f$ transition when our laser is perfectly resonant?**

We can consider taking the limit of the sinc^2 function with $\alpha \equiv \omega_{fi} - \omega \rightarrow 0$:

$$\lim_{\alpha \rightarrow 0} \left[\frac{\sin^2(\alpha t)}{\alpha^2} \right] = \frac{\left[\alpha t - (\alpha t)^3/3! + \cdots \right]^2}{\alpha^2} = t^2 + \cdots \tag{47}$$

$$\rightarrow \quad P_{f \leftarrow i}(t) \sim \frac{|V_{fi}|^2}{4\hbar^2} \, t^2 \tag{48}$$

The probability of transition with a perfectly on-resonance driving field is quadratic in t. It turns out that this result holds only for small t; otherwise our truncation of the Taylor expansion in Eqn. 47 won't be a good approximation. See Section 5 below for a treatment that goes beyond PT to capture the long-time behavior of a resonantly driven system.

(c) **What is the rate of resonant $i \rightarrow f$ transitions in the long-time limit?**

In observation (a) we noted that the lineshape of our transition grows narrower as the laser interaction time t increases. In the long time limit, $P_{f \leftarrow i}(\omega)$ becomes increasingly sharply peaked, which we can approximate with a delta function:

$$\lim_{t \rightarrow \infty} \frac{\sin^2 \left[\frac{1}{2}(\omega_{fi} - \omega)t \right]}{(\omega_{fi} - \omega)^2} = \frac{\pi t}{2} \cdot \delta(\omega_{fi} - \omega) \tag{49}$$

Note that the factor of $\pi t/2$ arises simply because by definition, a δ function must integrate to 1, while the integral of sinc^2 is given by:

$$\int_{-\infty}^{\infty} dx \, \frac{\sin^2(\alpha x)}{x^2} = \pi |\alpha| \qquad \rightarrow \qquad \int_{-\infty}^{\infty} d\omega \, \frac{\sin^2 \left(\frac{1}{2}(\omega_{fi} - \omega)t \right)}{(\omega_{fi} - \omega)^2} = \frac{\pi t}{2} \tag{50}$$

Referring back to Eqn. 44, we can write our long-time limit of the transition probability as:

$$P_{f \leftarrow i}(t) = \frac{\pi |V_{fi}|^2 t}{2\hbar^2} \, \delta(\omega_{fi} - \omega) \tag{51}$$

Since the probability scales linearly in t in this regime, we consider instead the transition *rate*, which is the transition probability per unit time:

$$\boxed{\Gamma_{fi} \equiv \frac{P_{f\leftarrow i}(t)}{t} = \frac{\pi |V_{fi}|^2}{2\hbar^2}\, \delta(\omega_{fi} - \omega)} \tag{52}$$

This is ***Fermi's Golden Rule*** describing the state-to-state transition rate.

5 A "large" sinusoidal perturbation

All of our work in Section 4 above assumed that our molecule was interacting with a field that was sufficiently weak that we remained within the perturbative regime as given by Eqn. 16. Put another way, we assumed that the field cannot drive a significant fraction of the probability distribution out of the initial $|\psi_i\rangle$ state. We'll now explore what happens when we go beyond PT under *strong* monochromatic radiation.

Let's go back to the step just before we invoked TDPT, pulling our expression from Eqn. 15:

$$i\hbar \dot{b}_k(t) = \sum_n b_n(t)\, H^{(1)}_{kn}(t)\, e^{i(\omega_k - \omega_n)t} \tag{53}$$

The $b_k(t)$ may change significantly in time, so we can no longer expand in powers of λ and truncate. Instead, we will work near resonance with $\omega = \omega_{fi}$, so only states $|\psi_i\rangle$ and $|\psi_f\rangle$ should contribute significantly to the dynamics. This is equivalent to reduucing our problem to a two-level system which we can handle explicitly. We will take the initial conditions $b_i(0) = 1$ and $b_f(0) = 0$.

Using Eqn. 53 to lay out a coupled system of differential equations for $b_f(t)$ and $b_i(t)$, we find:

$$i\hbar \dot{b}_f(t) = b_i(t)\, H^{(1)}_{fi}(t)\, e^{i\omega_{fi}t} \tag{54}$$

$$= b_i(t)\, \frac{V_{fi}}{2}\, \left[e^{i\omega t} + e^{-i\omega t}\right]\, e^{i\omega_{fi}t} \tag{55}$$

$$= b_i(t)\, \frac{V_{fi}}{2} \left[e^{i(\omega_{fi}+\omega)t} + e^{i(\omega_{fi}-\omega)t}\right] \tag{56}$$

$$i\hbar \dot{b}_i(t) = b_f(t)\, \frac{V_{if}}{2}\, \left[e^{i(\omega_{if}+\omega)t} + e^{i(\omega_{if}-\omega)t}\right] \tag{57}$$

We now make two simplifying approximations: **(a)** we take the laser near resonance with $\omega = \omega_{fi} = -\omega_{if}$ and **(b)** we invoke the rotating wave approximation to drop the $\pm\,(\omega_{fi}+\omega) = \pm 2\,\omega$ terms, which oscillate rapidly with respect to ω and will therefore "wash out" once integrated over:

$$i\hbar \dot{b}_f(t) = b_i(t)\, \frac{V_{fi}}{2}\, \left[e^{2i\omega t} + 1\right] \approxeq b_i(t)\, \frac{V_{fi}}{2} \tag{58}$$

$$i\hbar \dot{b}_i(t) = b_f(t)\, \frac{V_{if}}{2}\, \left[1 + e^{-2i\omega t}\right] \approxeq b_f(t)\, \frac{V_{if}}{2} \tag{59}$$

Finally, we solve this system of differential equations by taking a second time derivative and substituting Eqn. 59 into Eqn. 58:

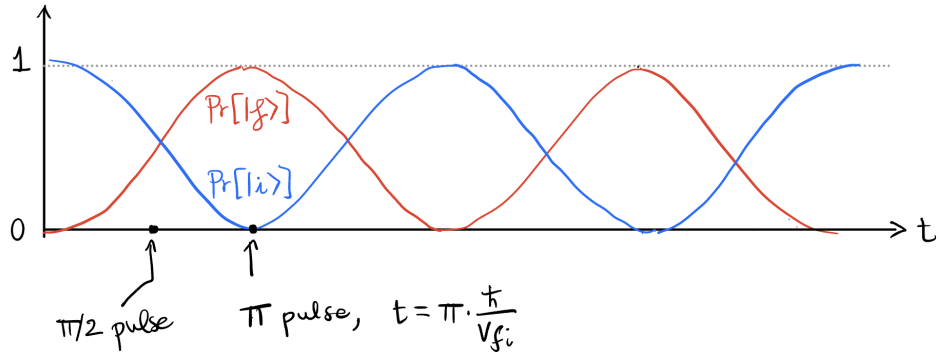
$$i\hbar\ddot{b}_f(t) = \dot{b}_i(t)\,\frac{V_{fi}}{2} = b_f(t)\,\frac{|V_{fi}|^2}{4i\hbar} \tag{60}$$

$$\rightarrow \quad b_f(t) = \sin\left[\frac{V_{fi}}{2\hbar}\,t\right] \qquad \text{assuming } b_f(0) = 0 \tag{61}$$

$$b_i(t) = \cos\left[\frac{V_{fi}}{2\hbar}\,t\right] \qquad \text{assuming } b_i(0) = 1 \tag{62}$$

We therefore find:

$$P_{f\leftarrow i}(t) = |b_f(t)|^2 = \sin^2\left[\frac{V_{fi}}{2\hbar}\,t\right] \tag{63}$$



These oscillating state weightings should look familiar; they look rather like the Rabi oscillations we saw in Module 4 for the probability of observing an eigenstate of the reference Hamiltonian of a two-level system subject to a time-independent perturbation. The underlying physics are different here – we are driving the system between reference states with a time-varying perturbation – but these are still dubbed Rabi oscillations or "Rabi flopping."

A few notes on how to understand this results:

(a) It should be clear from inspection why these dynamics cannot be captured by PT. The system is driven from $|\psi_i\rangle$ at time $t = 0$ fully into $|\psi_f\rangle$ and back again, as long as the radiation persists.

(b) The terms π-pulse and $\pi/2$ pulse may be familiar from NMR. We can see these concepts arise here. A π-pulse is a resonant cw field that is turned on for precisely the right length of time to coherently drive the system from $|\psi_i\rangle$ to $|\psi_f\rangle$. This occurs when $P_{f\leftarrow i}(t)$ is maximized, which is when the argument of the $\sin^2$ is equal to $\pi/2$:

$$\frac{V_{fi}}{2\hbar}\,t_\pi = \frac{\pi}{2} \quad \rightarrow \quad \boxed{t_\pi = \pi\frac{\hbar}{V_{fi}}} \tag{64}$$

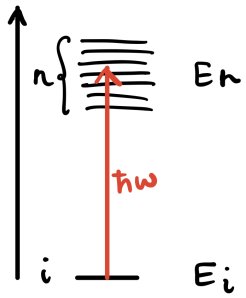
A $\pi/2$ pulse drives $|\psi_i\rangle$ into a coherent, 50:50 superposition state of $|\psi_i\rangle$ and $|\psi_f\rangle$:

$$\frac{V_{fi}}{2\hbar}\,t_{\pi/2} = \frac{\pi}{4} \quad \rightarrow \quad \boxed{t_{\pi/2} = \frac{\pi}{2}\frac{\hbar}{V_{fi}}} \tag{65}$$

(c) Note that if we Taylor expand Eqn. 63 in the short t limit, we return our weak-field TDPT finding that $P_{f\leftarrow i} = \frac{|V_{fi}|^2}{4\hbar^2}t^2$.

6 Bonus: Fermi's golden rule for transitions into a continuum

We finally consider inducing a transition into a manifold of closely spaced final states. What is the probability we make a transition from an initial state labeled i to *any* final state in our manifold under illumination with light at frequency ω?



We'll start by considering a manifold of discrete states. Let's use our TDPT result from Eqn. 44, but consider a sum over all potentially contributing states:

$$P_{f\leftarrow i}(t) = \sum_n \frac{|V_{ni}|^2}{\hbar^2}\left[\frac{\sin\left[\frac{1}{2}(\omega_{ni}-\omega)t\right]}{\omega_{ni}-\omega}\right]^2 \tag{66}$$

Where the index n labels all possible final states. We take the continuum limit of this expression by simply replacing the sum with an integral:

$$P_{f\leftarrow i}(t) = \int dn\, \frac{|V_{ni}|^2}{\hbar^2}\left[\frac{\sin\left[\frac{1}{2}(\omega_{ni}-\omega)t\right]}{\omega_{ni}-\omega}\right]^2 \tag{67}$$

The dn differential counts through the final states by some index, but its more useful to label final states by their energy instead:

$$dn = dE_n \cdot \rho(E_n) \tag{68}$$

where $\rho(E_n)$ gives the density of states per unit energy. We therefore have:

$$P_{f\leftarrow i}(t) = \int_{-\infty}^{\infty} dE_n \cdot \rho(E_n) \cdot \frac{|V_{ni}|^2}{\hbar^2}\left[\frac{\sin\left[\frac{1}{2}(\omega_{ni}-\omega)t\right]}{\omega_{ni}-\omega}\right]^2 \tag{69}$$

$$= \int_{-\infty}^{\infty} dE_n \cdot \rho(E_n) \cdot |V_{ni}|^2\left[\frac{\sin\left[\frac{1}{2}(E_n-E_i-\hbar\omega)t/\hbar\right]}{E_n-E_i-\hbar\omega}\right]^2 \tag{70}$$

Note that this integral is over states lying at *all* energies, though we expect only the states lying at energies near resonance with ω to contribute much, due to the sharply peaked envelope of the sinc^2 function.

This sharp distribution of sinc^2 lets us make a useful approximation. We will assume that both V_{ni} and $\rho(E_n)$ are constant over the narrow energy window of relevant near-resonant states. In

other words, the sharp sinc^2 function "plucks out" a constant value of these quantities at energy $E_f \equiv \hbar\omega$. This allows us to write:

$$P_{f\leftarrow i}(t) = 4|V_{fi}|^2 \rho(E_f) \int_{-\infty}^{\infty} dE_n \left[\frac{\sin(\frac{1}{2}(E_n - E_i - \hbar\omega)t/\hbar)}{(E_n - E_i - \hbar\omega)} \right]^2 \tag{71}$$

The remaining integral is straightforward to evaluate, using:

$$\int_{-\infty}^{\infty} dx \, \frac{\sin^2(\alpha x)}{x^2} = \pi|\alpha| \tag{72}$$

Using $x = E_n - E_i - \hbar\omega$ and $\alpha = \frac{t}{2\hbar}$, we find:

$$P_{f\leftarrow i}(t) = |V_{fi}|^2 \, \rho(E_f) \, \frac{\pi t}{2\hbar} \tag{73}$$

And again, this expression is linear in t, so it is most commonly expressed as the transition probability per unit time:

$$\boxed{\Gamma_{f\leftarrow i} = \frac{\pi}{2\hbar} \left| \langle \psi_f | \hat{V} | \psi_i \rangle \right|^2 \rho(E_f)} \tag{74}$$

This is a beautiful, surprisingly simple result. All we need to calculate the transition rate into a continuum of quantum states under monochromatic radiation is the perturbing matrix element connecting the two states, and the density of states at the transition frequency.