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

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We have now considered the effects of small, time-independent perturbations to various systems. But what happens when we have a time-dependent perturbation, for instance when we subject a molecule or atom to the oscillating electromagnetic field of a laser beam when we perform spectroscopy?

In time-independent perturbation theory we asked the question "what are the new eigenstates and eigenenergies of a perturbed system." In time-dependent perturbation theory (TDPT), it doesn't make much sense to ask about the eigenstates and eigenenerges of a system with a time-varying Hamiltonian. So instead, we phrase our driving question as "What is the probability that, some time t after a perturbation is applied, 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)?"

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 small parameter for bookkeeping.

Note that we assume our zeroth-order reference Hamiltonian $\hat{H}^{(0)}$ is time-independent, and its energy eigenstates $|\psi_n\rangle$ fulfill 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 can 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 $\hat{H}^{(1)}$ 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:

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

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

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

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

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 in time as well as more interesting dynamics due to the time-dependent 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 a couple of lectures back.)

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

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

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

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

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 coefficient is defined in terms of all others.

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

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

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

Here, $b_f^{(0)}$ 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:

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

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

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

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

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

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

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

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

And we can finally return to our initial desired quantity:

$$P_{f\leftarrow i}(t) = |c_f(t)|^2 = |e^{-i\omega_f t}|^2\cdot|\cancelto{0}{b_f^{(0)}} + \lambda b_f^{(1)}(t) + \cdots|^2 \approx \lambda^2|b_f^{(1)}(t)|^2 \tag{21}$$

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

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 to treat with TDPT is a perturbation that is switched on very slowly:

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

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

We initialize the system in $|\psi_i\rangle$ and want to find the probability that we end up in $|\psi_f\rangle$ at time t. We can find the time-dependent expansion coefficients of our wavefunction using Eqn. 20:

$$b_f^{(1)}(t) = \frac{1}{i\hbar} \int_0^t dt' \ \langle \psi_f | \hat{V}(1 - e^{-kt'}) | \psi_i \rangle \ e^{i\omega_{fi} t'} \tag{24}$$

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

$$= \frac{V_{fi}}{i\hbar} \int_0^t dt' \ \left[e^{i\omega_{fi} t} - e^{(i\omega_{fi} - k)t'} \right] \tag{26}$$

$$= \frac{V_{fi}}{i\hbar} \left[\frac{1}{i\omega_{fi}} \left[e^{i\omega_{fi} t} - 1 \right] - \frac{1}{i\omega_{fi} - k} \left[e^{i\omega_{fi} t} e^{-kt} - 1 \right] \right] \tag{27}$$

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

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

$$= -\frac{V_{fi} \cdot e^{i\omega_{fi} t}}{\hbar \omega_{fi}} = -\frac{V_{fi} \cdot e^{i\omega_{fi} t}}{E_f - E_i} = \frac{V_{fi} \cdot e^{i\omega_{fi} t}}{E_i - E_f} \tag{29}$$

$$\rightarrow \quad P_{f \leftarrow i} = |b_f^{(1)}(t)|^2 = \frac{|V_{fi}|^2}{(E_f - E_i)^2} \tag{30}$$

Eqn. 29 should look familiar: it's nearly identical to the expansion coefficients of the i^{th} first-order wavefunction in time-*independent* perturbation theory, where we found

$$c_{fi}^{(1)} = \frac{\hat{H}_{fi}^{(1)}}{E_i^{(0)} - E_f^{(0)}} \tag{31}$$

In our time-dependent case, $\hat{V}$ stands 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 new stationary states of the Hamiltonian at $t \to \infty$, which is given 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 instant* throughout the whole process.

This is 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. We 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

$$\underline{\hat{\mu}} = \sum_i q_i \cdot \underline{r_i} \tag{32}$$

which describes the spatial distribution of charges in the molecule.

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

$$\underline{E}(t) = \underline{\xi} \cos \omega t \tag{33}$$

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 perturbing time-dependent Hamiltonian as:

$$\hat{H}^{(1)} = \underline{\hat{\mu}} \cdot \underline{E}(t) = \underline{\hat{\mu}} \cdot \underline{\xi} \cos \omega t \equiv \frac{\hat{V}}{2} \left[e^{i\omega t} + e^{-i\omega t} \right] \tag{34}$$

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

$$b_f^{(1)}(t) = \frac{1}{i\hbar} \int_0^t dt' \ \langle \psi_f | \frac{\hat{V}}{2} \left[e^{i\omega t'} + e^{-i\omega t'} \right] | \psi_i \rangle \ e^{i\omega_{fi} t'} \tag{35}$$

$$= \frac{V_{fi}}{2i\hbar} \int_0^t dt' \left[e^{i\omega t'} + e^{-i\omega t'} \right] e^{i\omega_{fi} t'} \tag{36}$$

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

$$= \frac{V_{fi}}{2\hbar} \left[\frac{1 - e^{i(\omega_{fi}+\omega)t}}{(\omega_{fi} + \omega)} + \frac{1 - e^{i(\omega_{fi}-\omega)t}}{(\omega_{fi} - \omega)} \right] \tag{38}$$

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 will lead to 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 see absorption or stimulated emission of light. Spontaneous emission does not arise naturally out of first-order perturbation theory; more on this to come, too.

Let's now consider the resonant absorption case, where $\omega \approx \omega_{fi}$. In this limit, the second term of Eqn. 38 dominates as its denominator approaches zero, so we drop the first term entirely. We

find:

$$P_{f\leftarrow i}(t) = |b_f^{(1)}(t)|^2 = \frac{|V_{fi}|^2}{4\hbar^2}\left|\frac{1-e^{i(\omega_{fi}-\omega)t}}{\omega_{fi}-\omega}\right|^2 \tag{39}$$

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

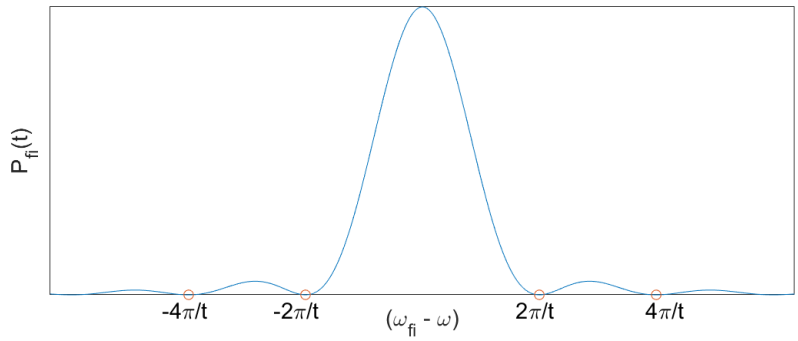
$$= \frac{|V_{fi}|^2}{4\hbar^2(\omega_{fi}-\omega)^2}\left[1-e^{i(\omega_{fi}-\omega)t}-e^{-i(\omega_{fi}-\omega)t}+1\right] \tag{41}$$

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

$$= \frac{|V_{fi}|^2}{4\hbar^2}\cdot\frac{4\sin^2(\frac{1}{2}(\omega_{fi}-\omega)t)}{(\omega_{fi}-\omega)^2} = \frac{|V_{fi}|^2}{4\hbar^2}\cdot\left[\frac{\sin(\frac{1}{2}(\omega_{fi}-\omega)t)}{\frac{1}{2}(\omega_{fi}-\omega)}\right]^2 \tag{43}$$

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 $\mathrm{sinc}(x) = \sin(x)/x$.



Let's use this distribution to make some observations:

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

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

$$\omega_{fi}-\omega = \pm 2n\pi/t \quad \text{for} \quad n = 1, 2, \cdots \tag{44}$$

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 width of the central resonance. This is a property of Fourier transforms: the accuracy with which you can determine the precise frequency of an oscillation improves the longer the period of time you have to observe it. This phenomenon is sometimes referred to as the time-energy uncertainty relation.

In our present case, we might handwave something like:

$$\Delta E = \hbar\Delta\omega \simeq \hbar\,\frac{4\pi}{\Delta t} \qquad \rightarrow \qquad \Delta E\Delta t \simeq 4\pi\hbar \tag{45}$$

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

Finally, note that everything we have derived here assumes a perfect continuous wave field and ignores any homogeneous or heterogeneous broadening of the molecular transitions. The sinc^2 lineshape comes only from the limited interaction time of the molecule in the field.

(b) **What is the probability of making the $i \rightarrow f$ transition perfectly on resonance?**

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

$$\lim_{\alpha\to 0}\left[\frac{\sin^2(\alpha t)}{\alpha^2}\right] = \frac{\left[\alpha t - (\alpha t)^3/3! + \cdots\right]^2}{\alpha^2} = t^2 + \cdots \tag{46}$$

$$\rightarrow \quad P_{f\leftarrow i}(t) \sim \frac{|V_{fi}|^2}{4\hbar^2}\,t^2 \tag{47}$$

It looks like 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. 46 won't be a good approximation.

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

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

$$\lim_{t\to\infty}\frac{\sin^2(\frac{1}{2}(\omega_{fi}-\omega)t)}{(\omega_{fi}-\omega)^2} = \frac{\pi t}{2}\cdot\delta(\omega_{fi}-\omega) \tag{48}$$

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:

$$\int_{-\infty}^{\infty} dx\,\frac{\sin^2(\alpha x)}{x^2} = \pi|\alpha| \qquad \rightarrow \qquad \int_{-\infty}^{\infty} d\omega\,\frac{\sin^2\left(\frac{1}{2}(\omega_{fi}-\omega)t\right)}{(\omega_{fi}-\omega)^2} = \frac{\pi t}{2} \tag{49}$$

Referring back to Eqn. 43, we can write our long-time limit of the transition probability as:

$$P_{f\leftarrow i}(t) = \frac{\pi|V_{fi}|^2 t}{2\hbar^2}\,\delta(\omega_{fi}-\omega) \tag{50}$$

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

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

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

5 A "large" sinusoidal perturbation

All of our work in the previous section assumed that our molecule was interacting with a field that was sufficiently weak or sufficiently short 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 the perturbative regime under *strong* monochromatic radiation.

To begin, let's go back to our last step before we invoked TDPT, pulling our expression from Eqn. 15:

$$i\hbar\dot{b}_k(t) = \sum_n b_n(t)\,\hat{H}^{(1)}_{kn}\,e^{i(\omega_k-\omega_n)t} \tag{52}$$

We can no longer expand each $b_k(t)$ in powers of λ and truncate, as they may change significantly in time.

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 essentially the two-level system picture which we can solve explicitly. We will take the initial conditions $b_i(0) = 1$ and $b_f(0) = 0$.

Evaluating Eqn. 52 for both $b_f(0)$ and $b_i(0)$, we find:

$$i\hbar\dot{b}_f(t) = b_i(t)\,\hat{H}^{(1)}_{fi}\,e^{i\omega_{fi}t} \tag{53}$$

$$= b_i(t)\,\frac{V_{fi}}{2}\,\left[e^{i\omega t} + e^{-i\omega t}\right]\,e^{i\omega_{fi}t} \tag{54}$$

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

$$i\hbar\dot{b}_i(t) = b_f(t)\,\frac{V_{if}}{2}\,\left[e^{i(\omega_{if}+\omega)t} + e^{i(\omega_{if}-\omega)t}\right] \tag{56}$$

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

$$i\hbar\dot{b}_f(t) = b_i(t)\,\frac{V_{fi}}{2}\,\left[e^{2i\omega t} + 1\right] \approxeq b_i(t)\,\frac{V_{fi}}{2} \tag{57}$$

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

Finally, we solve this system of differential equations by taking a second time derivative and substituting Eqn. 58 into Eqn. 57:

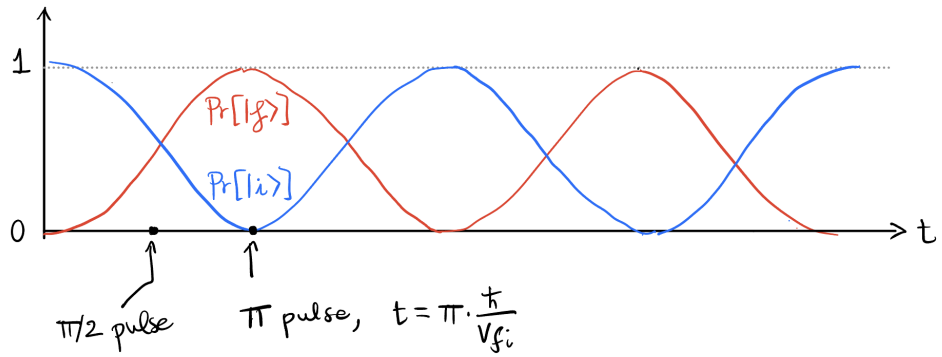
$$i\hbar\ddot{b}_f(t) = \frac{V_{fi}}{2}\,\dot{b}_i(t) = \frac{|V_{fi}|^2}{4i\hbar}\,b_f(t) \tag{59}$$

$$\rightarrow \quad b_f(t) = \sin\left[\frac{V_{fi}}{2\hbar}\,t\right] \qquad \text{assuming } b_f(0) = 0 \tag{60}$$

$$b_i(t) = \cos\left[\frac{V_{fi}}{2\hbar}\,t\right] \qquad \text{assuming } b_i(0) = 1 \tag{61}$$

We therefore find:

$$P_{f\leftarrow i}(t) = |b_f(t)|^2 = \sin^2\left[\frac{V_{fi}}{2\hbar}\,t\right] \tag{62}$$



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

A few final notes on how to understand these 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 experiments. We can see these concepts arise here.

A π-pulse is a resonant, continuous wave 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 when the argument of the sine^2 is equal to $\pi/2$:

$$\frac{V_{fi}}{2\hbar}\,t_\pi = \frac{\pi}{2} \quad \rightarrow \quad \boxed{t_\pi = \pi\frac{\hbar}{V_{fi}}} \tag{63}$$

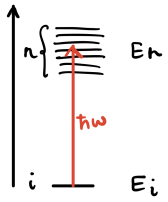
A $\pi/2$ pulse drives the system from $|\psi_i\rangle$ into a coherent, 50:50 superposition state of $|\psi_i\rangle$ and $|\psi_f\rangle$:

$$\frac{V_{fi}}{2\hbar}\,t_\pi = \frac{\pi}{4} \quad \rightarrow \quad \boxed{t_{\pi/2} = \frac{\pi}{2}\frac{\hbar}{V_{fi}}} \tag{64}$$

(c) Note that if we Taylor expand Eqn. 62 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. 43, but consider a sum over all potentially contributing states:

$$P_{f\leftarrow i}(t) = \sum_n \frac{|V_{ni}|^2}{\hbar^2}\left[\frac{\sin(\frac{1}{2}(\omega_{ni}-\omega)t)}{(\omega_{ni}-\omega)}\right]^2 \tag{65}$$

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:

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

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

$$dn = dE_n \cdot \rho(E_n) \tag{67}$$

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

$$P_{f\leftarrow i}(t) = \int_{-\infty}^{\infty} dE_n \cdot \rho(E_n) \cdot \frac{|V_{ni}|^2}{\hbar^2}\left[\frac{\sin(\frac{1}{2}(\omega_{ni}-\omega)t)}{(\omega_{ni}-\omega)}\right]^2 \tag{68}$$

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

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

$$P_{f\leftarrow i}(t) = 4|V_{fi}|^2\rho(E_f)\int_{-\infty}^{\infty} dE_n\left[\frac{\sin(\frac{1}{2}(E_n-E_i-\hbar\omega)t/\hbar)}{(E_n-E_i-\hbar\omega)}\right]^2 \tag{70}$$

The remaining integral is straightforward to evaluate, using:

$$\int_{-\infty}^{\infty} dx \, \frac{\sin^2(\alpha x)}{x^2} = \pi|\alpha| \tag{71}$$

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

$$P_{f\leftarrow i}(t) = |V_{fi}|^2 \, \rho(E_f) \, \frac{\pi t}{2\hbar} \tag{72}$$

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

$$\boxed{\Gamma_{f\leftarrow i} = \frac{\pi}{2\hbar} \left|\langle f|\hat{V}|i\rangle\right|^2 \rho(E_f)} \tag{73}$$

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