Monday: Found time-dependent transition probability amplitude:

$$C_{fi}^{(1)} = \frac{-i}{\hbar}\int_0^t dt' \exp\left[i(E_f - E_i)t'/\hbar\right] H'_{fi}(t)$$

So a time-dependent perturbation can produce a transition from one state of the unperturbed $\hat{H}_0$ to another, provided the matrix element of $\hat{H}'(t)$ between the initial and final states is nonzero. Things to note:

→ Behavior of transitions: Transition probability is "smoothed out" by the integral. So a sudden perturbation does <u>not</u> produce a sudden transition unless $H'_{fi}(t) = \infty$. We've actually already used this property: recall problems where the potential changes at $t=0$ but the wavefunction "doesn't have time to adjust."

Consider a delta function perturbation in time: $\hat{H}'_{fi}(t) = V_0 \delta(t)$.

$$C_{fi}^{(1)} = \frac{-iV_0}{\hbar}\int_0^t dt' \exp\left[i(E_f - E_i)t'/\hbar\right]\delta(t)$$

$$= \frac{-iV_0}{\hbar}$$

$$\longrightarrow P_{fi} = \left(\frac{V_0}{\hbar}\right)^2$$

which is obviously a bad approximation as $\frac{V_0}{\hbar} \gtrsim 1$.

Harmonic perturbations: application = electromagnetic radiation.

Assume $\hat{H}'$ is sinusoidal: $\hat{H}'(t) = \hat{V}\sin\omega t$, $\frac{\partial \hat{V}}{\partial t} = 0$.

Substitute into transition amplitude eqn:

$$C_{fi}(t) = \frac{-V_{fi}}{2\hbar}\int_0^t dt' \left[e^{i(\omega_{fi}+\omega)t'} - e^{i(\omega_{fi}-\omega')t}\right] \quad \text{where } \begin{array}{l} V_{fi} \equiv \langle f|\hat{V}|i\rangle \\ \omega_{fi} \equiv (E_f - E_i)\frac{1}{\hbar} \end{array}$$

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

and $|C_{fi}|^2 = P_{fi}(t)$ transition probability.

Brief comment on bound vs. free states: we derived this assuming discrete energies (bound states). So $P_{fi}$ is a real probability that oscillates as long as the perturbation is applied. For free particles (continuous energies) $P_{fi}$ is a probability density. Finally, for systems with bound and free states, if $|i\rangle$ is bound and $|f\rangle$ is free then the $P_{fi}$ is also a prob. density, but the transition to a free state is irreversible.

Back to bound-bound problem:

$$P_{fi}(t) = (4\hbar^2)^{-1}|V_{fi}|^2 |A_+ - A_-|^2 \quad \text{where}$$

$$A_\pm \equiv \frac{1-e^{i(\omega_{fi}\pm\omega)t}}{\omega_{fi}\pm\omega} = -ie^{i(\omega_{fi}\pm\omega)t/2}\,\frac{\sin[(\omega_{fi}\pm\omega)t/2]}{(\omega_{fi}\pm\omega)/2}$$

Note that denominator of $A_\pm$ vanishes for $\omega = \mp\omega_{fi}$ (but in the limit, fraction doesn't diverge.

So for $\omega \approx \omega_{fi}$, the $A_-$ term is dominant, if $\omega_{fi}t \gg 1$, and we find resonant behavior:

$$P_{fi}(t) \cong \frac{|V_{fi}|^2}{4\hbar^2}\left(\frac{\sin\left(\frac{(\omega_{fi}-\omega)t}{2}\right)}{(\omega_{fi}-\omega)/2}\right)^2 \qquad (*)$$

on resonance: $P_{fi}(t) = \frac{|V_{fi}|^2}{4\hbar^2}t^2$

Away from $\omega \approx \omega_{fi}$, $P_{fi}(t)$ decreases, going to zero at $|\omega - \omega_{fi}| = \frac{2\pi}{t}$ — then oscillates. Define resonance width $\Delta\omega = \frac{2\pi}{t}$ (Larger time $\leftrightarrow$ narrower width! Here's the $\Delta E \Delta t$ uncertainty principle showing its head again. Suppose you want to measure $\omega_{fi} = \frac{E_f - E_i}{\hbar}$ by applying a perturbation of tunable $\omega$ — as done in laser spectroscopy. If you apply it for an interval $\Delta t$, uncertainty $\Delta(E_f - E_i) = \hbar\Delta\omega \cong \hbar/\Delta t$.

Bound-Free transitions: $|f\rangle$ is in continuum energy regime.

$P_{fi} \to \frac{dP(E_f,t)}{dE}$ probability density per final energy. But Eq. $(*)$ remains valid, with the new interpretation. It's useful to take limit $t \to \infty$, and use identity $\lim_{t\to\infty} \frac{4}{\Delta^2}\sin^2\frac{\Delta t}{2} = 2\pi t\,\delta(\Delta)$

$$dP(E_f,t) = \frac{\pi t}{2\hbar}|V_{fi}|^2\delta(E_f - E_i - \hbar\omega)\,dE_f\,.$$

1st order transition probability grows linearly with $t$ for late times.

So, since the transition probability per unit time is linear, the transition rate is constant! "Fermi's golden rule"

$$\frac{d\Gamma}{dE_f} \equiv \frac{dP(E_f,t)}{dE_f\,dt} = \frac{\pi}{2\hbar}\left|\langle f|\hat{V}|i\rangle\right|^2 \delta(E_f - E_i - \hbar\omega)$$

Very important result in much of physics.

Usually integrate over a range of $E_f$, so $\delta$ disappears.