Wed: worked out transition probability for harmonic perturbation

$$\hat{H}' = \hat{V} \sin \omega t$$

For $\omega \approx \omega_{fi} = \frac{(E_i - E_f)}{\hbar}$, $\omega_{fi} t \gg 1$

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

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

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 $\Delta\omega = 2\pi/t$.

Aside: longer time = narrower width! Here's the $\Delta E \Delta t$ uncertainty principle raising its head again. Suppose you want to measure $\omega_{fi} = \frac{1}{\hbar}(E_f - E_i)$ by applying a perturbation with a tunable ω, as done in laser spectroscopy. If you apply it for an interval Δt, uncertainty $\Delta(E_f - E_i) = \hbar \Delta\omega \cong \hbar/\Delta t$. (Nice discussion on p. 482 of Shankar).

Bound-Free transitions: Assume $|i\rangle$ initial state is in discrete (bound) region, $|f\rangle$ is in (free) continuum.

Probability $P_{fi} \longrightarrow$ Probability density $\frac{dP(E_f, t)}{dE}$ per final energy.

Equation $(*)$ remains valid, but with a new interpretation. Useful to take limit of large time, and use identity

$$\lim_{t \to \infty} \frac{4}{\alpha^2} \sin^2\left(\frac{\alpha t}{2}\right) = 2\pi t \,\delta(\alpha)$$

So eq. (*) becomes

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

So, to 1st order, probability of transition increases linearly with time. Therefore, the rate of transition is constant, per unit time and energy:

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

This piece enforces energy conservation.

... which is known as Fermi's Golden Rule. Usually we integrate over a range of E_f, so the δ-function disappears. If final states are free-particle momentum eigenstates, then it becomes the density of states $\rho(E_f) = \frac{d^3p}{dE_f}$.

What happens in this sort of situation when the probability of transition approaches (or exceeds!) 1? In reality it is the "constant rate" argument that remains valid — the lifetime of the initial state has an exponential distribution from integrating $\frac{dP_i}{dt} = -\Gamma P_i$, where P_i is the probability $P_i = |\langle i|\psi(t)\rangle|^2$ that the system is still in state $|i\rangle$ at time t.

This is the generic behavior of a system where a perturbation couples a bound state to a continuum of free states. Common examples: radioactive decay, photoelectric effect.

Electromagnetic interactions. Motivation: photoelectric effect, radiative transitions.

Classical Hamiltonian:

$$\mathcal{H} = \frac{1}{2m}\left|\vec{p} + \frac{e}{c}\vec{A}\right|^2 - e\Phi$$

where $\vec{A}$ is the vector potential, Φ scalar potential so

$$\vec{E} = -\frac{1}{c}\frac{\partial \vec{A}}{\partial t} - \vec{\nabla}\Phi \;,\quad \vec{B} = \vec{\nabla}\times\vec{A}$$

Gaussian units

Physics should be insensitive to gauge. Work in the Coulomb gauge:

$$\vec{\nabla}\cdot\vec{A} = 0.$$

Now, find the potential for a plane wave: (in z-direction)

$$\left.\begin{aligned}\vec{E}(\vec{r},t) &= E_0 \sin(kz-\omega t)\,\vec{e}_x \\ \vec{B}(\vec{r},t) &= E_0 \sin(kz-\omega t)\,\vec{e}_y\end{aligned}\right\}$$

Note that E, B have the same units (gauss).

In Coulomb gauge, vector potential is

$$\vec{A} = \vec{A}_0 \cos(kz-\omega t)\,,\quad \vec{A}_0 = \frac{cE_0}{\omega}\vec{e}_x\,,\quad \Phi = 0.$$

Photoelectric effect: Take incoming wave on a hydrogen atom:

$$\vec{A}(\mathbf{r},t) = A_0\cos(k\cdot r - \omega t)$$

For some frequencies, electron will be liberated into a free energy level. Calculate rate using Golden Rule:

$$\hat{H}'(t) = \frac{-(-e)}{2mc}\left(\hat{\vec{A}}\cdot\hat{\vec{P}} + \hat{\vec{P}}\cdot\hat{\vec{A}}\right) \leftarrow$$

Need to do this because $\hat{p}$ and $\hat{A}$ don't commute ($\hat{A}$ depends on $\hat{\vec{r}}$)

$$\hat{H}_0(t) = \frac{\hat{p}^2}{2m} - \frac{e^2}{r}$$

So $\hat{H}'(t) = \frac{e}{2mc}\left(\hat{\vec{A}}\cdot\hat{\vec{P}} + \hat{\vec{P}}\cdot\hat{\vec{A}}\right)$

Now recall that Coulomb gauge has useful property $\vec{\nabla}\cdot\vec{A} = 0$

So $\hat{\vec{A}}\cdot\hat{\vec{P}} = \hat{\vec{P}}\cdot\hat{\vec{A}}$!

$$\hat{H}'(t) = \frac{e}{mc}\hat{\vec{A}}\cdot\hat{\vec{P}}$$

$$= \frac{e}{2mc}\left(e^{i(\vec{k}\cdot\hat{\vec{r}} - \omega t)} + e^{-i(\vec{k}\cdot\hat{\vec{r}} - \omega t)}\right)\vec{A}_0\cdot\hat{\vec{P}}$$

$e^{+i\omega t}$ term can't contribute to transition probability because of $\delta(E_f - E_i - \hbar\omega)$ factor.

Ignoring $e^{+i\omega t}$ term,

$$\hat{H}'(t) = \frac{e}{2mc}e^{i\vec{k}\cdot\hat{\vec{r}}}\hat{\vec{A}}_0\cdot\hat{\vec{p}}\,e^{-i\omega t} = \hat{V}(r)e^{-i\omega t}$$

... which is indeed a harmonic perturbation.

We'll complete derivation on Monday.