

- Last time: write the SE: $i\hbar\partial_t|\psi(t)\rangle = (H_0 + H_1(t))|\psi(t)\rangle$ and expand in the basis of eigenstates of H_0 : $|\psi(t)\rangle = \sum_n a_n(t)e^{-iE_n^{(0)}t}|n^0\rangle$, and then the SE gives $0 = \sum_n (i\hbar\dot{a}_n(t) - H_1(t)a_n(t))e^{-iE_n^{(0)}t}|n^0\rangle$ and then get $i\hbar\dot{a}_f = \sum_n \langle f^0|H_1(t)|n^0\rangle e^{i\omega_{fn}t} a_n(t)$, where $\omega_{fn} = (E_f^0 - E_n^0)/\hbar$. Now expand in perturbative series. If at time $t = 0$ the system is in state $|i^0\rangle$ then the first order result is

$$a_f(t) = \delta_{fi} - \frac{i}{\hbar} \int_0^t \langle f^0|H_1(t')|i^0\rangle e^{i\omega_{fi}t'} dt' + \mathcal{O}(H_1^2).$$

- Recall from last time the interaction picture: $|\psi_I(t)\rangle = e^{iH_0t/\hbar}|\psi_S(t)\rangle$, with time evolution $|\psi_I(t)\rangle = U_I(t, t_0)|\psi_I(t_0)\rangle$ and $i\hbar\frac{d}{dt}U_I = H_I(t)U_I$. This leads to the integral equation $U_I(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t H_1(t')U_I(t', t_0)dt'$. Integrate to $U_I = T \exp(-(i/\hbar) \int dt' H_I(t'))$. Can expand, or iterate the integral equation, to get the Dyson series.

- For a sudden perturbation, over time $\Delta t \rightarrow 0$, integrating the SE gives $\Delta|\psi\rangle = \frac{i}{\hbar}\Delta t H(t)|\psi\rangle \rightarrow 0$, so the state is unchanged. E.g. a particle in a box whose size suddenly grows from L to L' , if it was originally in the groundstate, compute the probability to find it in the new groundstate.

The opposite limit is an adiabatic perturbation, where if the rate of change is slow enough the system will go from an eigenstate $|n(0)\rangle$ of $H(0)$ to the corresponding eigenstate $|n(\tau)\rangle$ of $H(\tau)$. E.g. particle in a box where the walls slowly expand. E.g. also $H_1(t) = H_1(0)e^{-t^2/\tau^2}$, from $t = -\infty$ to $t = \infty$. Can verify that for $\omega\tau \gg 1$ the system in an eigenstate at $t = -\infty$ will be in the same eigenstate for $t = +\infty$.

Expand $\psi = \sum_n a_n(t)u_n(t) \exp((i\hbar)^{-1} \int_0^t E_n(t')dt')$ where $H(t)u_n(t) = E_n(t)u_n(t)$. Can show (see e.g. Schiff) that $\dot{a}_{k \neq n} \approx (\hbar\omega_{kn})^{-1} \langle k|\dot{H}|n\rangle e^{i\omega_{kn}t}$, which does not grow with time.

- Case $H_1(t) = H_1\Theta(t)$, get $a_n^{(1)} = \frac{-i}{\hbar} V_{ni} \int_0^t e^{i\omega_{ni}t'} dt' = V_{ni}(1 - e^{i\omega_{ni}t})/(E_n - E_i)$ so $|a_n^{(1)}|^2 = (4|V_{ni}|^2/(E_n - E_i)^2) \sin^2((E_n - E_i)t/2\hbar)$, where all $E_{n,i}$ are the H_0 eigenvalues (I'm dropping the 0 subscript or superscript reminder of that). Recall what $\text{sinc}^2(x) \equiv \sin^2 x/x^2$ looks like: peak is 1 (at $x = 0$) and it integrates to π , with central peak for $|x| \leq \pi$. So the transition probability has peak proportional to t^2 and width proportional to $1/t$. For large t , it is appreciable only in the central peak, i.e. $|E_n - E_i|t \leq 2\pi\hbar$, which is roughly like a $\Delta E \Delta t$ analog of the $\Delta x \Delta p \geq \hbar/2$ uncertainty relation (except the interpretation is different (t is a parameter vs x as an operator) and the inequality is opposite).

- When there is a continuum of possible final states, we replace $\sum_n \rightarrow \int dE_n \rho(E_n)$. E.g. for a particle in a box of volume V with periodic boundary conditions we have $\sum_{\vec{n}} \rightarrow \int (V/(2\pi)^3) d^3\vec{p}$ and $d^3\vec{p} = p^2 dp d\Omega_p$ and then do a change of variables to $E = p^2/2m$, gives $\rho(E) = (mV/(2\pi\hbar)^3) E d\Omega_p$.

- The golden rule: for $t \rightarrow \infty$, $(E_n - E_i)^{-2} \sin^2((E_n - E_i)t/2\hbar) \rightarrow (\pi t/2\hbar) \delta(E_n - E_i)$. So $\int_n P_{n_0 \rightarrow n}(t) = \int dE_n \rho(E_n) P_{n_0 \rightarrow n}(t) \rightarrow \Gamma_{i \rightarrow n} t$ with

$$\Gamma_{i \rightarrow n} = \frac{2\pi}{\hbar} (\rho(E_n) |\langle n | H_1 | i \rangle|^2) |_{E_n \rightarrow E_i}.$$

Fermi called it the golden rule number 2; it was first obtained by Dirac.

We can similarly get the golden rule if the perturbation acts from $-T/2$ to $+T/2$, taking $T \rightarrow \infty$: get $a_f = -\hbar^{-1} 2\pi i V_{fi} \delta(\omega_{fi} - \omega)$. To compute the probability need to square the delta function: $\delta^2 = \lim_{T \rightarrow \infty} \delta(\omega_{fi} - \omega) \int_{-T/2}^{T/2} e^{i(\omega_{fi} - \omega)t} dt / 2\pi \rightarrow \delta(\omega_{fi} - \omega) T / 2\pi$. We need to divide by 2π and compute a rate to get a sensible answer.

Working to 2nd order, the result differs by replacing $|V_{ni}|^2 \rightarrow |V_{ni} + \sum_{m \neq i} \frac{V_{nm} V_{mi}}{E_i - E_m}|^2$. This can be pictured in terms of the perturbation taking $|i\rangle$ to an intermediate *virtual* state $|m\rangle$.

- Consider harmonic $H_1(t)$, taking $H_1(t) = H_1 e^{-i\omega t} + h.c.$. Then get to first order $a_f^1(t) = \hbar^{-1} (\frac{1 - e^{i(\omega + \omega_{ni})t}}{\omega + \omega_{ni}} V_{ni} + \frac{1 - e^{i(\omega_{ni} - \omega)t}}{-\omega + \omega_{ni}} V_{ni}^\dagger)$. Compared with the previous case, we need to replace $\omega_{ni} \rightarrow \omega_{ni} \pm \omega$. For $t \rightarrow \infty$ the amplitude is appreciable only for $E_n \approx E_i \pm \hbar\omega$, i.e. the perturbation can lead to absorption or emission of energy $\hbar\omega$. For $t \rightarrow \infty$, if there is a continuum of energies, the golden rule becomes $\Gamma_{i \rightarrow n} = \frac{2\pi}{\hbar} (\rho(E_n) |\langle n | H_1 | i \rangle|^2) |_{E_n = E_i \pm \hbar\omega}$.

- Example of interaction with a classical radiation field: take $H_1 = e\phi - \frac{e}{mc} \vec{A} \cdot \vec{p}$ in Coulomb gauge $\nabla \cdot \vec{A} = 0$ and $\vec{A} = 2A_0 \hat{\epsilon} \cos(\vec{k} \cdot \vec{x} - \omega t)$, so harmonic with $V_{ni}^\dagger = -(eA_0/mc) (e^{i\vec{k} \cdot \vec{x}} \hat{\epsilon} \cdot \vec{p})_{ni}$. The absorption cross section is then (energy)(rate)/(energy flux), where the energy is $\hbar\omega$ and the flux is $(c/2)(E^2 + B^2)/8\pi = \omega^2 |A_0|^2 / 2\pi c$. Get

$$d\sigma_{abs} \approx 4\pi^2 \hbar m^2 \omega \frac{e^2}{\hbar c} |\langle n | e^{i\vec{k} \cdot \vec{x}} \hat{\epsilon} \cdot \vec{p} | i \rangle|^2 \rho(E_n) |_{E_n = E_i + \hbar\omega}.$$

In the dipole approximation, we replace $e^{i\vec{k} \cdot \vec{x}} \approx 1$ (good approximation for $\hbar\omega \sim Ze^2/R_{atom}$: higher terms suppressed by powers of $Z/137$). Also, use $\vec{p} = m[\vec{x}, H_0]/i\hbar$ to replace $(\hat{\epsilon} \cdot \vec{p})_{ni} \rightarrow im\omega_{ni} \hat{\epsilon} \cdot (\vec{x})_{ni}$.

- Einstein (today, in addition to being the day that Hawking died, and Pi day, is Einstein's birthday!) A and B coefficients (1917): the probability for spontaneous emission B and the probability of stimulated emission A must have ratio $B/A = \rho(\omega)$ in order

for equilibrium to be possible. Recall that the thermal average number of photons of frequency ω is $\overline{n(\omega)} = \sum_{n=0}^{\infty} n e^{-n\hbar\omega/k_B T} / \sum_n e^{-n\hbar\omega/k_B T} = (e^{\hbar\omega/k_B T} - 1)^{-1}$ Bose-Einstein distribution. Suppose that the walls of the cavity are made of atoms with two energy levels, of energy E_1 and $E_2 > E_1$, then $P_2/P_1 = e^{-(E_2-E_1)/k_B T}$ is the thermal probability ratio of the states. Spontaneous absorption and emission gives $\dot{n}_1 = -Bn_1P_1$ and $\dot{n}_2 = Bn_2P_2$. If these were the only effects, all photons would be absorbed because $P_2 < P_1$. There must be an additional, stimulated emission process to obtain balance. The stimulated emission rate, due to the perturbation, is $\dot{n}_1 = A_{21}n_2\rho(\omega)$ for emission and $\dot{n}_1 = -A_{12}n_1\rho(\omega)$ for absorption. Balancing gives $0 = B_{21}n_2 + A_{21}n_2\rho(\omega) - A_{12}n_1\rho(\omega)$. Using $n_i = w_i e^{-E_i/k_B T} / Z$ the balancing requires $A_{21}/A_{12} = w_1/w_2$ (state multiplicity ratio), and $B_{21}/A_{21} = 2\hbar\omega^3/\pi c^3$. The emission and absorption process could be studied using time-dependent perturbation theory with a harmonic perturbation of frequency ω , in the dipole approximation. The spontaneous and stimulate emission is related to the fact that photons should be written in terms of creation and annihilation operators $a_{\vec{p}}^\dagger$ and $a_{\vec{p}}$ which are similar to those of the SHO for each frequency mode. Then $a_{\omega}^\dagger |n_\omega\rangle = \sqrt{n_\omega + 1} |n_\omega + 1\rangle$. The 1 term gives the spontaneous piece and the $n(\omega)$ term gives the stimulated piece. We ran out of time and could not discuss it here. See e.g. Baym for more details.