Time-Dependent Perturbation Theory

- General Problem + Formal Solution
  - Hamiltonian is $H = H_0 + H_1(t)$
    - + H_0 is time-independent, and we know e'states
    - + $H_1(t)$ "turns on" at $t=0$.
  - If the system starts in a stationary state $|\psi_i^0\rangle$ of H_0 at $t=0$,
    - + what is the state at time t?
    - + Another phrasing: what is the probability you would measure the system in a different H_0 stationary state $|\psi_f^0\rangle$ at t? (what is the <u>transition probability</u>?)
    - + Note that there is never a transition between stationary states except for the additional time dependence. This is ultimately related to MRI, excited state decay, etc
  - We write the state in the basis of H_0 e'states
    $$|\Psi(t)\rangle = \sum_n c_n(t)\exp(-iE_n^0 t/\hbar)\,|\psi_n^0\rangle$$
    - + This has the H_0 time dependence in the exponential and additional time dependence in $c_n(t)$
    - + Normalization is $\sum_n |c_n(t)|^2 = 1$
    - + Typical initial conditions are in a single e'state of H_0
      $$c_{\bar{n}}(0) = 1 \quad , \quad c_{n\neq\bar{n}}(0) = 0$$
  - The Schr. Eqn is
    $$\left(i\hbar\frac{d}{dt} - H\right)|\Psi(t)\rangle = \sum_n \left(i\hbar\,\dot{c}_n - c_n H_1\right)|\psi_n^0\rangle e^{-iE_n^0 t/\hbar} = 0$$
    $\Rightarrow$
    $$\dot{c}_n = \frac{-i}{\hbar}\sum_m \langle\psi_n^0|H_1|\psi_m^0\rangle\, c_m\, e^{-i(E_m^0 - E_n^0)t/\hbar} \qquad (*)$$
    after an inner product. This is <u>exact</u>.
  - First Order Perturbation Theory
    - + With our initial conditions, $c_{\bar{n}}(t) = 1 + c_{\bar{n}}^1(t)$, $c_{n\neq\bar{n}}(t) = c_n^1(t)$
      That is, the other states are all 1st order
    - + Then $(*)$ becomes (note H_1, c_n^1 1st order)
      $$\dot{c}_{\bar{n}} = \frac{-i}{\hbar}\langle\psi_{\bar{n}}^0|H_1|\psi_{\bar{n}}^0\rangle, \quad \dot{c}_{n\neq\bar{n}} = \frac{-i}{\hbar}\langle\psi_n^0|H_1|\psi_{\bar{n}}^0\rangle e^{-i(E_{\bar{n}}^0 - E_n^0)t/\hbar}$$

+ The 1st order solution is

$$c_{\bar n}(t) = 1 - i/\hbar \int_0^t dt' \langle \psi_{\bar n}^0 | H_1(t') | \psi_{\bar n}^0 \rangle$$

and

$$c_{n\neq \bar n} = -i/\hbar \int_0^t dt' \langle \psi_n^0 | H_1(t') | \psi_{\bar n}^0 \rangle \exp\left[-i(E_{\bar n}^0 - E_n^0)t'/\hbar\right]$$

Can work out the normalization

- Sinusoidal Perturbations

• As a very important example, take $H_1(t) = Ve^{-i\omega t} + V^\dagger e^{+i\omega t}$ with V = constant operator

+ Could take the form

$$H_1(t) = V \begin{bmatrix} 0 & e^{\pm i\omega t} \\ e^{\mp i\omega t} & 0 \end{bmatrix} \quad \text{or} \quad H_1 \propto \sin(\omega t), \quad H_1 \propto \cos(\omega t)$$

+ At linear order, we can consider the effects of only a single complex exponential at a time. Take $e^{-i\omega t}$

+ Note: GS uses cosine time-dependence, so we differ by factor of 2 in definition of V.

• For simplicity, we focus on 2 states $n = 1, 2$ with $\bar n = 1$

+ We also assume

$$\langle 1|V|1\rangle = \langle 2|V|2\rangle = 0, \quad V_{21} \equiv \langle 2|V|1\rangle = \langle 1|V^\dagger|2\rangle^*$$

+ The energy difference defines a natural frequency

$$E_2^0 - E_1^0 \equiv \hbar\omega_0$$

• Our solution is

$$c_1(t) = 1, \quad c_2(t) = (V_{21}/\hbar)\, \frac{e^{i(\omega_0-\omega)t} - 1}{\omega_0 - \omega}$$

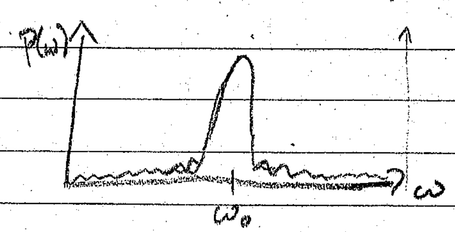
+ This is small except for $\omega \approx \omega_0$

+ The $e^{+i\omega t}$ term is the same with $\omega \to -\omega$, $V_{21} \to V_{12}^*$. But it is large near $\omega \approx -\omega_0$, and we ignore it near $\omega \approx \omega_0$

• The transition probability is the probability of measuring state 2

+ That is

$$P = |\langle 2|\Psi(t)\rangle|^2 = |c_2(t)|^2 = \left(\frac{4|V_{21}|^2}{\hbar^2}\right) \frac{\sin^2[(\omega_0-\omega)t/2]}{(\omega_0-\omega)^2}$$



+ There is a peak at $\omega = \omega_0$ (and a corresponding one at $\omega = -\omega_0$)

+ Away from the peak, $P(\omega)$ falls off quickly and oscillates in time

+ At the peak, L'Hospital's rule gives $P(\omega_0) = |V_{21}|^2 t^2 / \hbar^2$ which grows in time.

+ But the total integral $\int_{-\infty}^{\infty} d\omega\ P(\omega) = \left(\frac{4|V_{21}|^2}{\hbar^2}\right)\left(\frac{t}{2}\right)\pi$

(from $\int dx \sin^2 x / x^2 = \pi$ by Parseval's theorem for Fourier transforms)

+ An infinitely high peak with finite area is a δ function, so

$$P(\omega) \rightarrow \frac{2\pi|V_{21}|^2}{\hbar^2}\, t\, \delta(\omega - \omega_0)$$

This formula is called Fermi's Golden Rule and gives a constant transition rate (per unit time)

(GS gives a different discussion)

- Application to EM radiation (GS discussion is heuristic only)
  - You learned in 3301 that the interaction of a charge with EM field is given by

$$H = \frac{1}{2m}(\vec{p} - q\vec{A})^2 + q\Phi$$

+ The fields are

$$\vec{E} = -\vec{\nabla}\Phi - \partial\vec{A}/\partial t, \quad \vec{B} = \vec{\nabla}\times\vec{A}$$

+ For a particle in a potential (say Coulomb for hydrogen) interacting with an EM wave, we take

$$H_0 = \frac{\vec{p}^2}{2m} + q\Phi_0, \quad H_1 = \frac{-q}{2m}(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}) + \frac{q^2}{2m}\vec{A}^2 + q\Phi_1$$

where

Φ_0 = electrostatic potential, $\vec{A}$ & Φ_1 = small 1st order parts

- An EM wave can be described by

$$\Phi_1 = 0, \quad \vec{A} = \vec{A}_0 \exp[i(\vec{k}\cdot\vec{x} - \omega t)] \text{ + conjugate} \quad \text{with } \vec{\nabla}\cdot\vec{A} = 0 \Rightarrow \vec{p}\cdot\vec{A} = \vec{A}\cdot\vec{p}$$

+ This is where GS handwaves a bit, but there are math tricks that make it agree with us

+ Suppose the wavelength of the wave is long compared to the size of our quantum system (ie, the atom). Then $\vec{k}\cdot\vec{x} \simeq 0$ and

$H_1 \propto (q/m)\,\vec{A}_0 \cdot \vec{p}\, e^{-i\omega t}$ (plus conjugate)

+ Note that the $\vec{A}^2$ term is smaller.
+ This Hamiltonian gives the electric dipole transition

• Types of transitions

+ This term in H_1 leads to a transition of the electronic state from $|\psi_1^0\rangle \to |\psi_2^0\rangle$ with $E_2^0 - E_1^0 = \hbar\omega_0 = \hbar\omega$ by the golden rule. This is absorption (to higher energy)
+ The conjugate term swaps $\omega \to -\omega$, so the transition loses energy $E_2^0 - E_1^0 = \hbar\omega_0 = -\hbar\omega$. This is called stimulated emission, meaning the electron emits energy due to a passing EM field.
+ There is also spontaneous emission. This is due to a hidden time dependence in the quantum theory of EM fields.

• Selection rules

+ The electric dipole transition probability for an atomic state, for ex. hydrogen, goes like
$$|\langle n', l', m' | \vec{p} | n, l, m \rangle|^2$$
+ Based on the rotational symmetry, this is zero unless
$$l' - l = \pm 1 \quad \text{and} \quad m' - m = 0 \text{ or } \pm 1$$
These are selection rules & follow from the Wigner-Eckart theorem found in Chapter 6.
+ Some states can only decay through suppressed transitions from including more terms from $e^{i\vec{k}\cdot\vec{x}}$ for example.