



NPTEL ONLINE CERTIFICATION COURSES

Approximate Methods in Quantum Chemistry

Sabyashachi Mishra
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Lecture 38: Time-Dependent Perturbation Theory - I

Time-dependent Schrödinger Equation

$$\hat{H}\Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}$$

The wavefunction evolves in *time* according to the time-dependent Schrödinger equation

Separation of spatial and temporal variables

$$\Psi(x, t) = \psi(x)f(t)$$

$$\hat{H}\psi(x)f(t) = i\hbar f(t) \frac{\partial \psi(x)}{\partial t} + i\hbar \psi(x) \frac{\partial f(t)}{\partial t}$$

$$f(t)\hat{H}\psi(x) = i\hbar \psi(x) \frac{\partial f(t)}{\partial t}$$

$$\frac{1}{\psi(x)} \hat{H}\psi(x) = i\hbar \frac{1}{f(t)} \frac{\partial f(t)}{\partial t}$$

$$\hat{H}\psi(x) = E\psi(x)$$

$$i\hbar \frac{1}{f(t)} \frac{\partial f(t)}{\partial t} = E \Rightarrow f(t) \propto e^{-iEt/\hbar}$$



Stationary State

$$\Psi_n(x, t) = \psi_n(x)e^{-iE_nt/\hbar} = \psi_n(x)e^{-i\omega_nt}$$

$$|\Psi_n(x, t)|^2 = |\psi_n(x)|^2$$

$$\langle \hat{H} \rangle = \langle \Psi_n(x, t) | \hat{H} | \Psi_n(x, t) \rangle = \langle \psi_n(x) | \hat{H} | \psi_n(x) \rangle$$

States with a specific and precise energy and in which the potential energy does not vary with time are in *stationary states*.



Non-stationary State

Consider a state defined by an arbitrary function

$$\Psi(x, t) = \sum_n c_n \psi_n(x) e^{-i\omega_n t}$$

$$|\Psi(x, t)|^2 = \sum_n |c_n|^2 |\psi_n(x)|^2 + \sum_n \sum_{m \neq n} c_n^* c_m \psi_n^* \psi_m e^{i(\omega_n - \omega_m)t}$$

$$c_k = \langle \psi_k(x) | \Psi(x, t_0) \rangle e^{i\omega_k t_0}$$



Time-dependent Perturbation Theory

Hamiltonian with explicit time-dependence

$$\hat{H} = \hat{H}^{(0)} + \hat{H}'(t)$$

$$\hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$$

$$\Psi_n^{(0)}(x, t) = \psi_n^{(0)} e^{-i\omega_n^{(0)}t}$$

Consider a two-state system

$$\Psi(x, t) = c_1(t)\Psi_1^{(0)}(x, t) + c_2(t)\Psi_2^{(0)}(x, t)$$

$$\hat{H}\Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}$$

$$(\hat{H}_0 + \hat{H}') \left(c_1 \Psi_1^{(0)} + c_2 \Psi_2^{(0)} \right) = i\hbar \frac{\partial}{\partial t} \left(c_1 \Psi_1^{(0)} + c_2 \Psi_2^{(0)} \right)$$



Time-dependent Perturbation Theory

$$(\hat{H}_0 + \hat{H}') (c_1 \Psi_1^{(0)} + c_2 \Psi_2^{(0)}) = i\hbar \frac{\partial}{\partial t} (c_1 \Psi_1^{(0)} + c_2 \Psi_2^{(0)})$$

$$c_1 \hat{H}_0 \Psi_1^{(0)} + c_2 \hat{H}_0 \Psi_2^{(0)} + c_1 \hat{H}' \Psi_1^{(0)} + c_2 \hat{H}' \Psi_2^{(0)} = i\hbar \left(c_1 \frac{\partial \Psi_1^{(0)}}{\partial t} + c_2 \frac{\partial \Psi_2^{(0)}}{\partial t} + \Psi_1^{(0)} \frac{\partial c_1}{\partial t} + \Psi_2^{(0)} \frac{\partial c_2}{\partial t} \right)$$

$$c_1 \hat{H}' \Psi_1^{(0)} + c_2 \hat{H}' \Psi_2^{(0)} = i\hbar \dot{c}_1 \Psi_1^{(0)} + i\hbar \dot{c}_2 \Psi_2^{(0)}$$

$$c_1 \hat{H}'(t) \psi_1^{(0)} e^{-i\omega_1 t} + c_2 \hat{H}'(t) \psi_2^{(0)} e^{-i\omega_2 t} = i\hbar \dot{c}_1 \psi_1^{(0)} e^{-i\omega_1 t} + i\hbar \dot{c}_2 \psi_2^{(0)} e^{-i\omega_2 t}$$



Time-dependent Perturbation Theory

$$c_1 \hat{H}'(t) \psi_1^{(0)} e^{-i\omega_1 t} + c_2 \hat{H}' \psi_2^{(0)} e^{-i\omega_2 t} = i\hbar \dot{c}_1 \psi_1^{(0)} e^{-i\omega_1 t} + i\hbar \dot{c}_2 \psi_2^{(0)} e^{-i\omega_2 t}$$

$$c_1 \left\langle \psi_1^{(0)} \left| \hat{H}'(t) \right| \psi_1^{(0)} \right\rangle e^{-i\omega_1 t} + c_2 \left\langle \psi_1^{(0)} \left| \hat{H}'(t) \right| \psi_2^{(0)} \right\rangle e^{-i\omega_2 t} = \\ i\hbar \dot{c}_1 \left\langle \psi_1^{(0)} \left| \psi_1^{(0)} \right\rangle e^{-i\omega_1 t} + i\hbar \dot{c}_2 \left\langle \psi_1^{(0)} \left| \psi_2^{(0)} \right\rangle e^{-i\omega_2 t}$$

$$c_1 H'_{11}(t) e^{-i\omega_1 t} + c_2 H'_{12}(t) e^{-i\omega_2 t} = i\hbar \dot{c}_1 e^{-i\omega_1 t}$$

$$c_2 H'_{22}(t) e^{-i\omega_2 t} + c_1 H'_{21}(t) e^{-i\omega_1 t} = i\hbar \dot{c}_2 e^{-i\omega_2 t}$$





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Approximate Methods in Quantum Chemistry

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Lecture 39: Time-Dependent Perturbation Theory - II

Time-dependent Perturbation Theory

Hamiltonian with explicit time-dependence

$$\hat{H} = \hat{H}^{(0)} + \hat{H}'(t)$$

$$\hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)}$$

$$\Psi_n^{(0)}(x, t) = \psi_n^{(0)} e^{-i\omega_n^{(0)}t}$$

Consider a two-state system

$$\Psi(x, t) = c_1(t)\Psi_1^{(0)}(x, t) + c_2(t)\Psi_2^{(0)}(x, t)$$

$$\hat{H}\Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}$$



Time-dependent Perturbation Theory

$$c_1 H'_{11}(t) e^{-i\omega_1 t} + c_2 H'_{12}(t) e^{-i\omega_2 t} = i\hbar \dot{c}_1 e^{-i\omega_1 t}$$

$$c_2 H'_{22}(t) e^{-i\omega_2 t} + c_1 H'_{21}(t) e^{-i\omega_1 t} = i\hbar \dot{c}_2 e^{-i\omega_2 t}$$

$$\begin{pmatrix} H'_{11}(t) & H'_{12}(t) \\ H'_{21}(t) & H'_{22}(t) \end{pmatrix} = \begin{pmatrix} 0 & H'_{12}(t) \\ H'_{21}(t) & 0 \end{pmatrix}$$

$$\dot{c}_1 = \frac{1}{i\hbar} c_2 H'_{12}(t) e^{-i\omega_{21} t}$$

$$\dot{c}_2 = \frac{1}{i\hbar} c_1 H'_{21}(t) e^{i\omega_{21} t}$$

Probability of finding the system in a particular state at a particular time

$$|c_1(t)|^2 = P_1(t)$$

$$|c_2(t)|^2 = P_2(t)$$

In the absence of perturbation $\hat{H}' = 0$

$$\dot{c}_1 = \frac{1}{i\hbar} c_2 H'_{12}(t) e^{-i\omega_{21}t}$$

$$\dot{c}_2 = \frac{1}{i\hbar} c_1 H'_{21}(t) e^{i\omega_{21}t}$$

$$\dot{c}_1 = \dot{c}_2 = 0$$

$$\Psi(x, t) = c_1(0) \psi_1^{(0)}(x) e^{-i\omega_1^{(0)}t} + c_2(0) \psi_2^{(0)}(x) e^{-i\omega_2^{(0)}t}$$

While the wavefunction oscillates with time, the coefficients do not change.
The state of the system is frozen at its initial composition.



Constant perturbation

$$\hat{H}'(t) = \hbar V$$

$$\dot{c}_1 = \frac{1}{i\hbar} c_2 H'_{12}(t) e^{-i\omega_{21}t}$$

$$\dot{c}_2 = \frac{1}{i\hbar} c_1 H'_{21}(t) e^{i\omega_{21}t}$$

$$\frac{d}{dt}c_1 = -ic_2 V e^{-i\omega_{21}t}$$

$$\frac{d}{dt}c_2 = -ic_1 V e^{i\omega_{21}t}$$

$$\ddot{c}_2 = i\omega_{21}\dot{c}_2 - |V|^2 c_2$$

General solution of the differential equation

$$c_2(t) = (Ae^{i\Omega t} + Be^{-i\Omega t}) e^{i\omega_{21}t/2} \quad \Omega = \frac{1}{2} \sqrt{\omega_{21}^2 + 4|V|^2}$$



Constant perturbation

$$\hat{H}'(t) = \hbar V$$

$$c_2(t) = (Ae^{i\Omega t} + Be^{-i\Omega t}) e^{i\omega_{21}t/2} \quad \Omega = \frac{1}{2} \sqrt{\omega_{21}^2 + 4|V|^2}$$

$$\dot{c}_1 = \frac{1}{i\hbar} c_2 H'_{12}(t) e^{-i\omega_{21}t}$$

$$\dot{c}_2 = \frac{1}{i\hbar} c_1 H'_{21}(t) e^{i\omega_{21}t}$$

Initial condition: $c_1(0) = 1 \quad c_2(0) = 0$

$$c_1(t) = \left(\cos \Omega t + \frac{i\omega_{21}}{2\Omega} \sin \Omega t \right) e^{-i\omega_{21}t/2}$$

$$c_2(t) = -\frac{i|V|}{\Omega} \sin \Omega t e^{i\omega_{21}t/2}$$

$$P_2(t) = |c_2(t)|^2 = \frac{|V|^2}{\Omega^2} \sin^2 \Omega t = \left(\frac{4|V|^2}{\omega_{21}^2 + 4|V|^2} \right) \sin^2 \frac{1}{2} \left(\sqrt{\omega_{21}^2 + 4|V|^2} \right) t$$

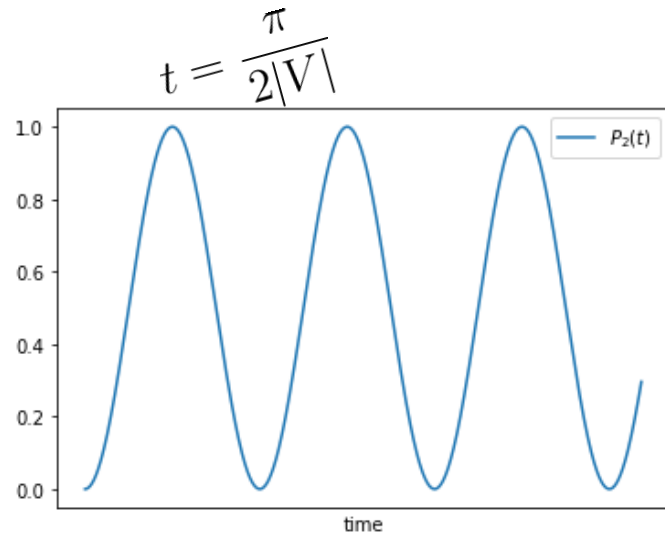
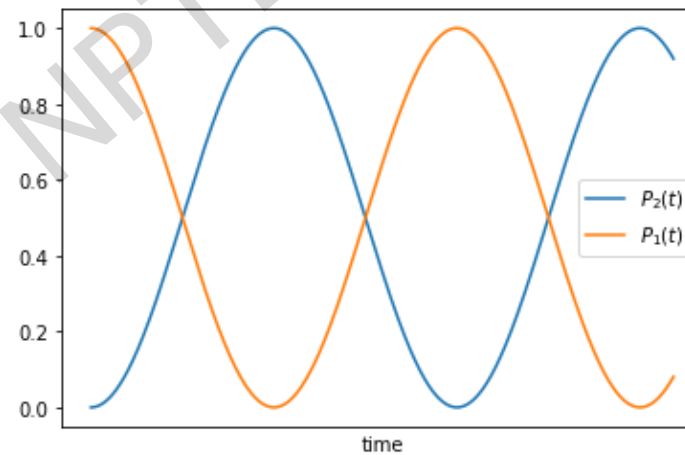


Rabi's Formula

$$P_2(t) = \left(\frac{4|V|^2}{w_{21}^2 + 4|V|^2} \right) \sin^2 \frac{1}{2} \left(\sqrt{w_{21}^2 + 4|V|^2} \right) t$$

Special Case 1: $w_{21} = 0$

$$P_2(t) = \sin^2 |V|t$$

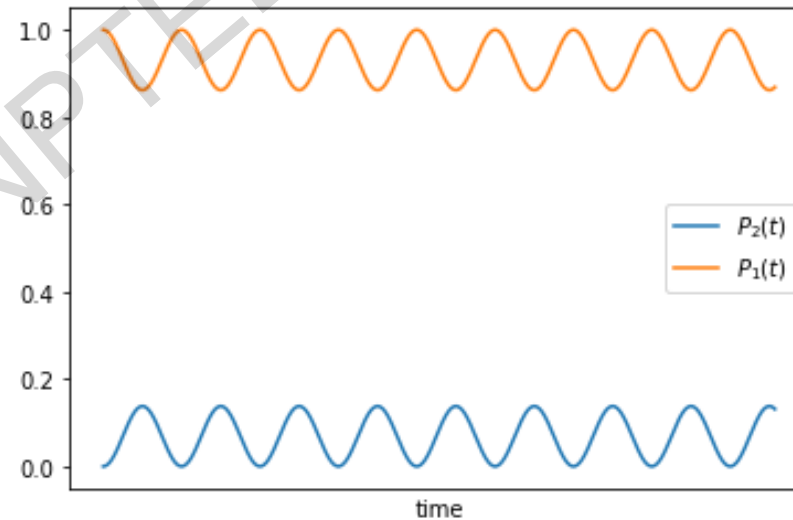


Rabi's Formula

$$P_2(t) = \left(\frac{4|V|^2}{w_{21}^2 + 4|V|^2} \right) \sin^2 \frac{1}{2} \left(\sqrt{w_{21}^2 + 4|V|^2} \right) t$$

Special Case 2: $\omega_{21}^2 \gg 4|V|^2$

$$P_2(t) = \left(\frac{4|V|^2}{w_{21}^2} \right) \sin^2 \frac{\omega_{21}}{2} t$$



Time-dependent behavior of multi-state systems

$$\hat{H} = \hat{H}^{(0)} + \hat{H}'(t)$$

Unperturbed system

$$\hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} = \hbar\omega_n^{(0)}\psi_n^{(0)}$$

$$\Psi_n^{(0)}(x, t) = \psi_n^{(0)}e^{-i\omega_n^{(0)}t} \quad \hat{H}^{(0)}\Psi_n^{(0)}(x, t) = i\hbar\frac{\partial\Psi_n^{(0)}(x, t)}{\partial t}$$

Final nonstationary state
as a linear combination

$$\Psi(x, t) = \sum_n c_n(t)\Psi_n^{(0)}(x, t) = \sum_n c_n(t)\psi_n^{(0)}e^{-i\omega_n^{(0)}t}$$

$$\hat{H}\Psi(x, t) = i\hbar\frac{\partial\Psi(x, t)}{\partial t}$$

$$(\hat{H}_0 + \hat{H}') \left(\sum_n c_n(t)\Psi_n^{(0)}(x, t) \right) = i\hbar\frac{\partial}{\partial t} \left(\sum_n c_n(t)\Psi_n^{(0)}(x, t) \right)$$

Time evolution of the states

$$\dot{c}_k(t) = \frac{1}{i\hbar} \sum_n c_n(t) H'_{kn} e^{i\omega_{kn}t}$$





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Lecture 40: Slowly Switched Constant Perturbation

Time-independent Systems

Stationary State

$$\Psi_n(x, t) = \psi_n(x)e^{-iE_nt/\hbar} = \psi_n(x)e^{-i\omega_nt}$$

$$|\Psi_n(x, t)|^2 = |\psi_n(x)|^2$$

Non-stationary State

$$\Psi(x, t) = \sum_n c_n \psi_n(x) e^{-i\omega_n t}$$

$$|\Psi(x, t)|^2 = \sum_n |c_n|^2 |\psi_n(x)|^2 + \sum_n \sum_{m \neq n} c_n^* c_m \psi_n^* \psi_m e^{i(\omega_n - \omega_m)t}$$

$$c_k = \langle \psi_k(x) | \Psi(x, t_0) \rangle e^{i\omega_k t_0}$$

Time-independent coefficients



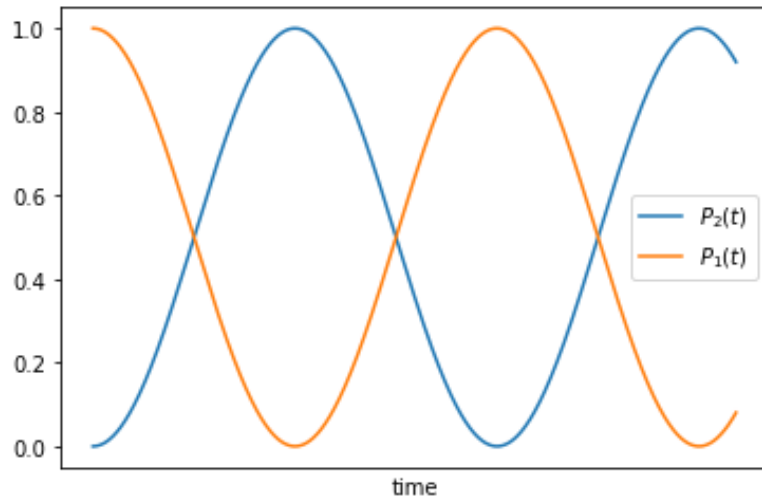
Time-dependent behavior of a two-state system

Rabi's Formula

$$P_2(t) = \left(\frac{4|V|^2}{w_{21}^2 + 4|V|^2} \right) \sin^2 \frac{1}{2} \left(\sqrt{w_{21}^2 + 4|V|^2} \right) t$$

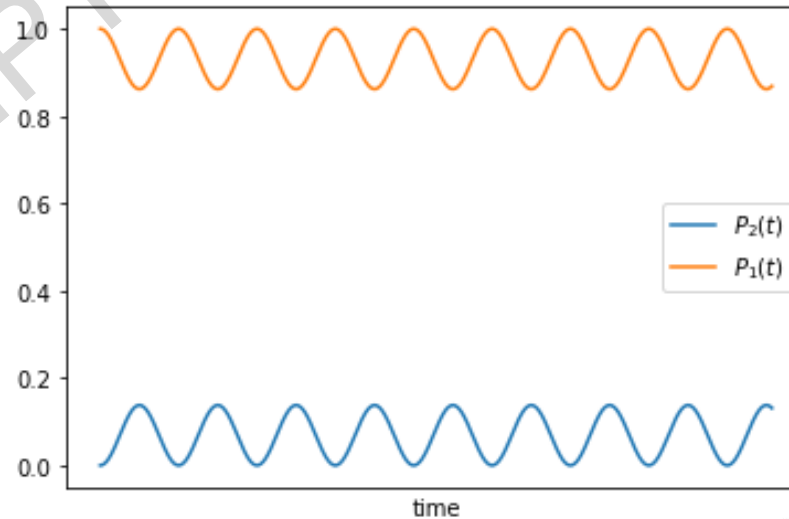
Special Case 1: $w_{21} = 0$

$$P_2(t) = \sin^2 |V|t$$



Special Case 2: $w_{21}^2 \gg 4|V|^2$

$$P_2(t) = \left(\frac{4|V|^2}{w_{21}^2} \right) \sin^2 \frac{w_{21}}{2} t$$



Time-dependent behavior of multi-state systems

Unperturbed system

$$\hat{H} = \hat{H}^{(0)} + \hat{H}'(t)$$
$$\hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} = \hbar\omega_n^{(0)}\psi_n^{(0)}$$

$$\Psi_n^{(0)}(x, t) = \psi_n^{(0)}e^{-i\omega_n^{(0)}t} \quad \hat{H}^{(0)}\Psi_n^{(0)}(x, t) = i\hbar\frac{\partial\Psi_n^{(0)}(x, t)}{\partial t}$$

Final nonstationary state as a linear combination

$$\Psi(x, t) = \sum_n c_n(t)\Psi_n^{(0)}(x, t) = \sum_n c_n(t)\psi_n^{(0)}e^{-i\omega_n^{(0)}t}$$

$$\hat{H}\Psi(x, t) = i\hbar\frac{\partial\Psi(x, t)}{\partial t}$$

$$(\hat{H}_0 + \hat{H}') \left(\sum_n c_n(t)\Psi_n^{(0)}(x, t) \right) = i\hbar\frac{\partial}{\partial t} \left(\sum_n c_n(t)\Psi_n^{(0)}(x, t) \right)$$

Time evolution of the states

$$\dot{c}_k(t) = \frac{1}{i\hbar} \sum_n c_n(t) H'_{kn} e^{i\omega_{kn}t}$$

$$H'_{kn} = \langle k | \hat{H}' | n \rangle$$
$$\hbar\omega_{kn} = \hbar\omega_k - \hbar\omega_n$$



Time-dependent behavior of multi-state systems

Time evolution of the states

$$\dot{c}_k(t) = \frac{1}{i\hbar} \sum_n c_n(t) H'_{kn} e^{i\omega_{kn}t}$$

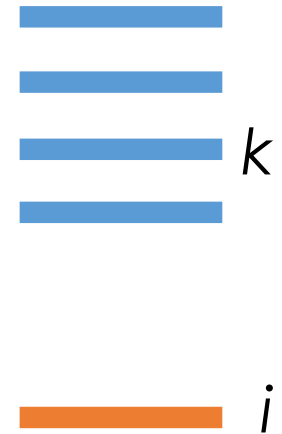
$$c_k(t) - c_k(0) = \frac{1}{i\hbar} \sum_n \int_0^t dt c_n(t) H'_{kn}(t) e^{i\omega_{kn}t}$$

- Weak perturbation
- Applied for a short time

$$c_f(t) = \frac{1}{i\hbar} \int_0^t dt c_i(t) H'_{fi}(t) e^{i\omega_{fi}t}$$

$$c_f(t) = \frac{1}{i\hbar} \int_0^t dt H'_{fi}(t) e^{i\omega_{fi}t}$$

Discards all indirect routes of transfer to final state from the initial state



Constant Perturbation – slowly switched

$$c_f(t) = \frac{1}{i\hbar} \int_0^t dt H'_f(t) e^{i\omega_{fi}t}$$

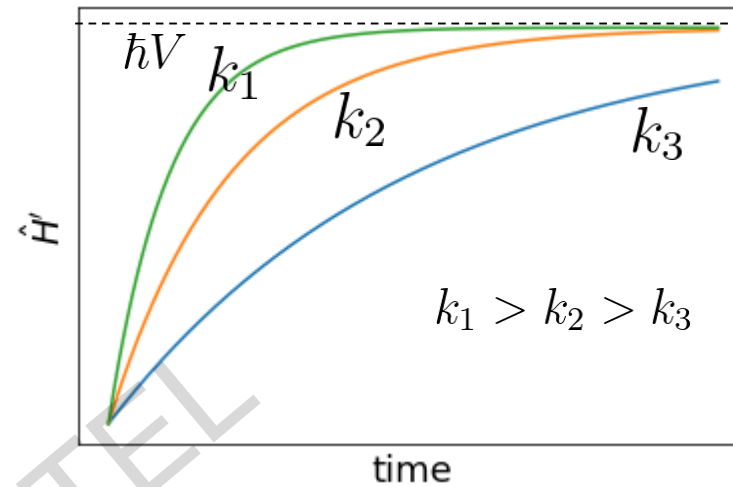
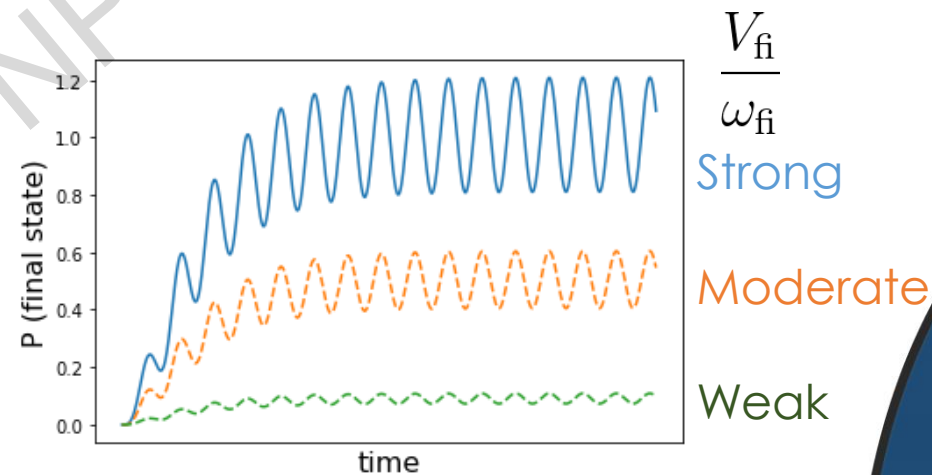
$$\hat{H}'(t) = \begin{cases} 0 & \text{for } t < 0 \\ \hbar V (1 - e^{-kt}) & \text{for } t \geq 0 \end{cases}$$

$$\begin{aligned} c_f(t) &= \frac{1}{i\hbar} \hbar V_{fi} \int_0^t dt (1 - e^{-kt}) e^{i\omega_{fi}t} \\ &= \frac{1}{i} V_{fi} \left(\frac{e^{i\omega_{fi}t} - 1}{i\omega_{fi}} - \frac{e^{-(k-i\omega_{fi})t} - 1}{k - i\omega_{fi}} \right) \end{aligned}$$

$$P_f(t) = |c_f(t)|^2$$

At time long after perturbation,

$$P_f(t) = \left(\frac{V_{fi}}{\omega_{fi}} \right)^2 = \left(\frac{\langle f | \hat{H}' | i \rangle}{E_f - E_i} \right)^2$$

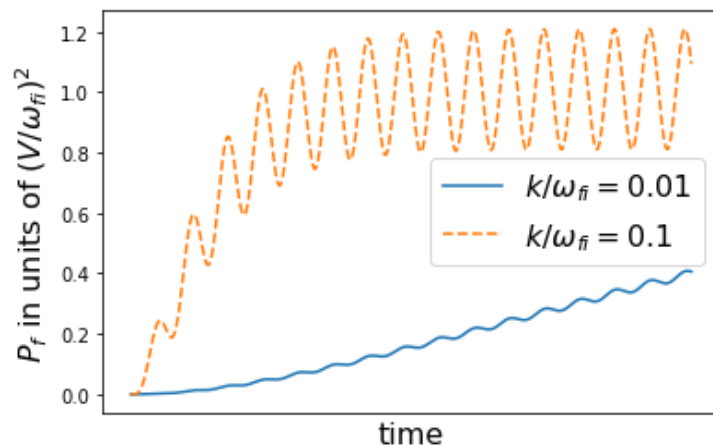
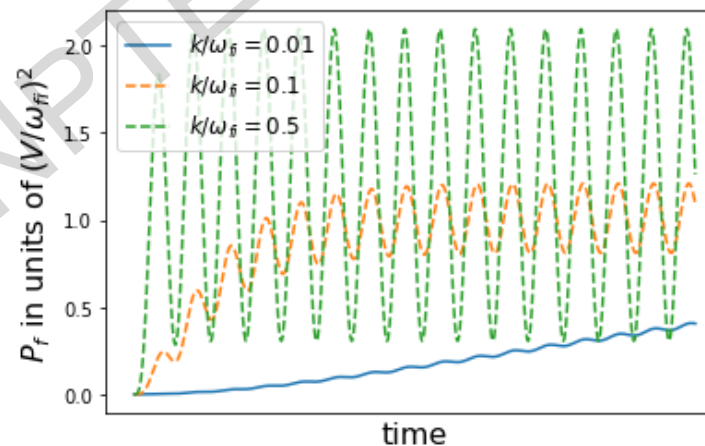
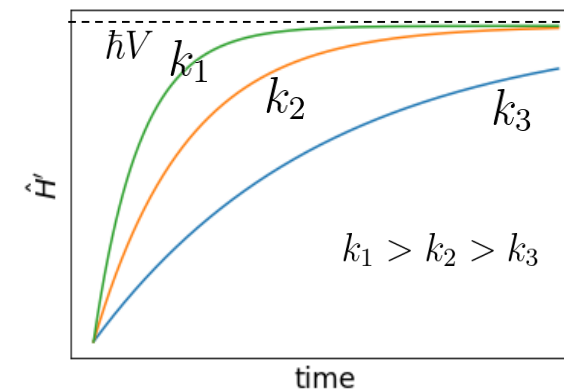


Constant Perturbation – slowly switched

$$\hat{H}'(t) = \begin{cases} 0 & \text{for } t < 0 \\ \hbar V (1 - e^{-kt}) & \text{for } t \geq 0 \end{cases}$$

$$P_f(t) = \left| \frac{1}{i} V_{fi} \left(\frac{e^{i\omega_{fi}t} - 1}{i\omega_{fi}} - \frac{e^{-(k-i\omega_{fi})t} - 1}{k - i\omega_{fi}} \right) \right|^2$$

Role of $\frac{k}{\omega_{fi}}$



At long time scale (for slowly switched perturbation) time-dependent perturbation results in steady population of states.



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Lecture 41: Oscillating Perturbation

Oscillating Perturbation

$$\hat{H}'(t) = \hbar V \cos \omega t = \hbar V (e^{i\omega t} + e^{-i\omega t}) \quad \text{for } t \geq 0$$

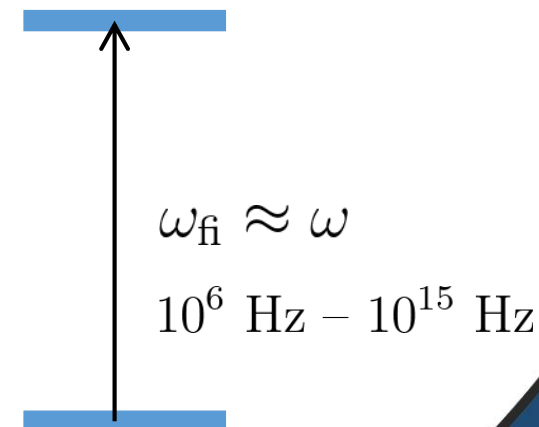
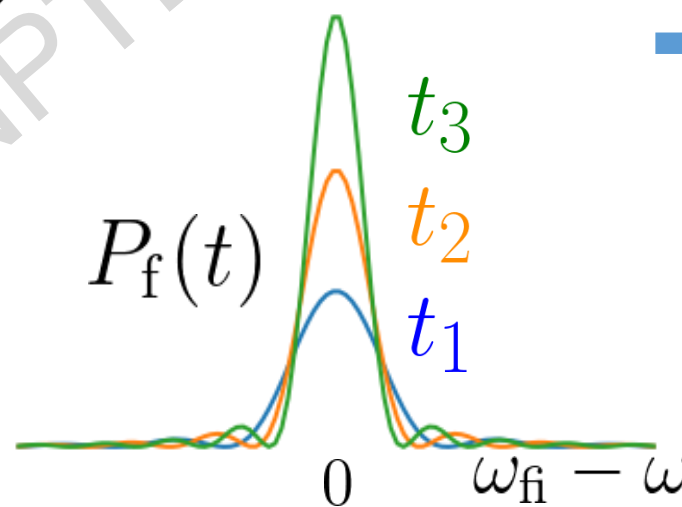
$$\begin{aligned} c_f(t) &= \frac{1}{i\hbar} \hbar V_{fi} \int_0^t dt (e^{i\omega t} + e^{-i\omega t}) e^{i\omega_{fi}t} \\ &= \frac{1}{i} V_{fi} \left(\frac{e^{i(\omega_{fi} + \omega)t} - 1}{i(\omega_{fi} + \omega)} + \frac{e^{i(\omega_{fi} - \omega)t} - 1}{i(\omega_{fi} - \omega)} \right) \end{aligned}$$

$$P_f(t) = 4V_{fi}^2 \frac{\sin^2 \frac{1}{2} (\omega_{fi} - \omega) t}{(\omega_{fi} - \omega)^2}$$

$$\lim_{x \rightarrow 0} \frac{\sin x}{x} = 1 \quad x = \frac{(\omega - \omega_{fi})t}{2}$$

$$\lim_{\omega \rightarrow \omega_{fi}} P_f(t) = V_{fi}^2 t^2$$

$$c_f(t) = \frac{1}{i\hbar} \int_0^t dt H'_{fi}(t) e^{i\omega_{fi}t}$$



Transition to a state in continuum

Total transition probability,

$$P(t) = \int P_f(t) \rho(E) dE$$

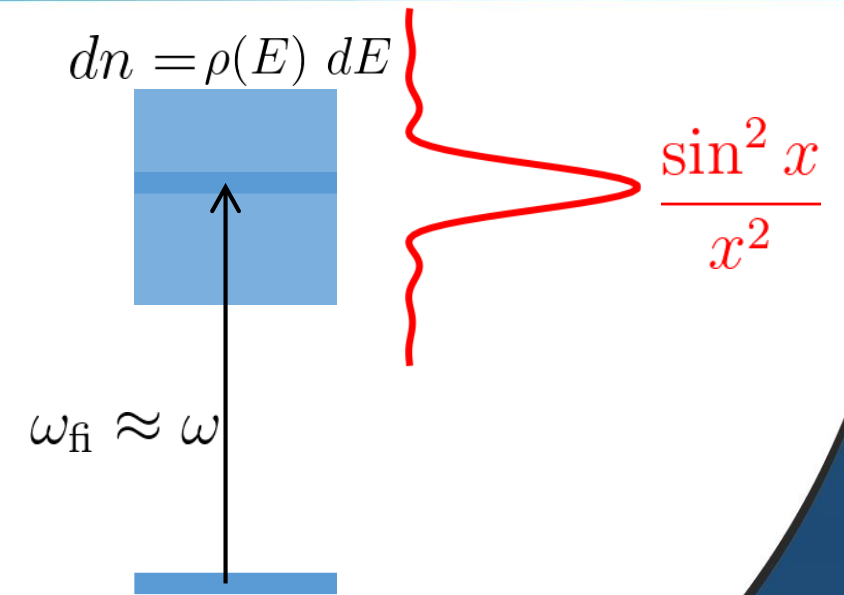
$$= \int 4V_{fi}^2 \frac{\sin^2 \frac{1}{2} (E/\hbar - \omega) t}{(E/\hbar - \omega)^2} \rho(E) dE$$

$$= V_{fi}^2 \rho(E_{fi}) \int \frac{4 \sin^2 \frac{1}{2} (E/\hbar - \omega) t}{(E/\hbar - \omega)^2} dE$$

$$= \left(\frac{2\hbar}{t} \right) t^2 V_{fi}^2 \rho(E_{fi}) \int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} dx$$

$$P(t) = 2\pi\hbar t V_{fi}^2 \rho(E_{fi})$$

$$P_f(t) = 4V_{fi}^2 \frac{\sin^2 \frac{1}{2} (\omega_{fi} - \omega) t}{(\omega_{fi} - \omega)^2}$$



$$x = \frac{1}{2} \left(\frac{E}{\hbar} - \omega \right) t \Rightarrow dx = \frac{t}{2\hbar} dE$$

Transition Rate (W)

The rate of change of the transition probability of an initially empty state

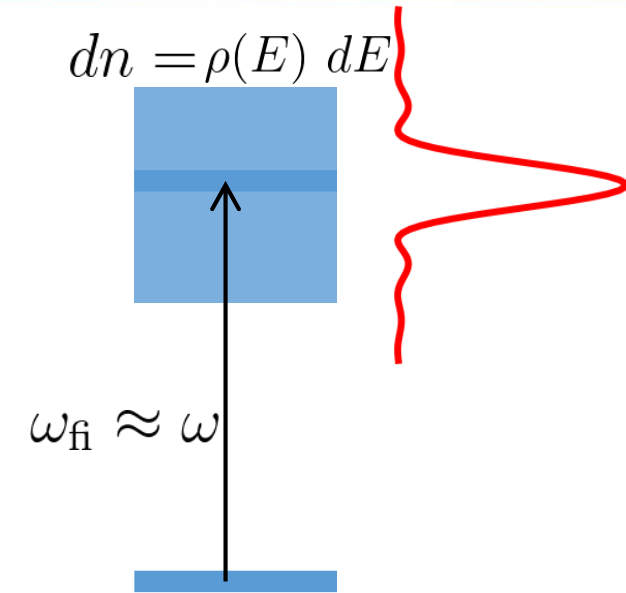
$$P(t) = 2\pi\hbar t V_{\text{fi}}^2 \rho(E_{\text{fi}})$$

Fermi's Golden Rule

$$W_{\text{f} \leftarrow \text{i}} = \frac{dP(t)}{dt} = 2\pi\hbar V_{\text{fi}}^2 \rho(E_{\text{fi}})$$

Spectral intensity: A measure of the rate of transfer of energy between matter and electromagnetic field

1. Transition matrix element
2. Density of states at the transition frequency





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Lecture 42: Einstein's Coefficients

Transition Rate (W)

The rate of change of the transition probability of an initially empty state

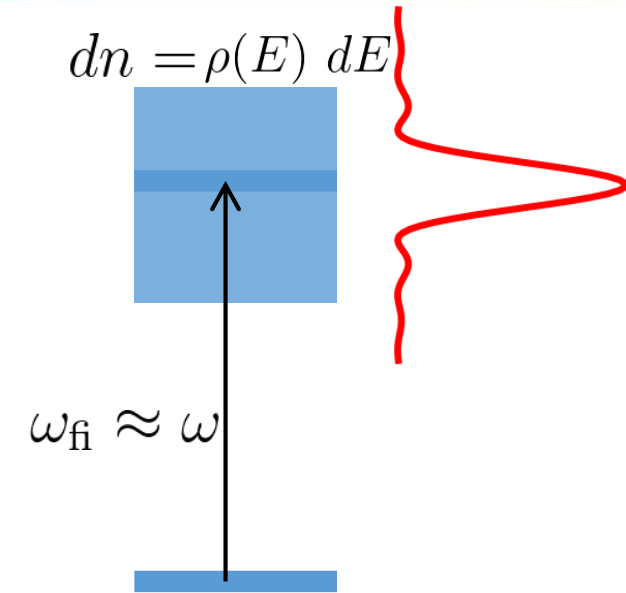
$$P(t) = 2\pi\hbar t V_{fi}^2 \rho(E_{fi})$$

Fermi's Golden Rule

$$W_{f \leftarrow i} = \frac{dP(t)}{dt} = 2\pi\hbar V_{fi}^2 \rho(E_{fi})$$

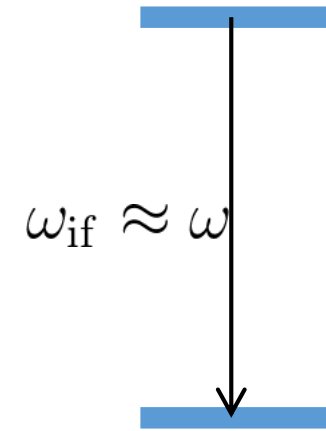
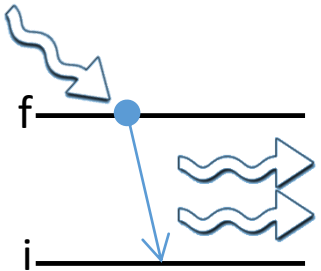
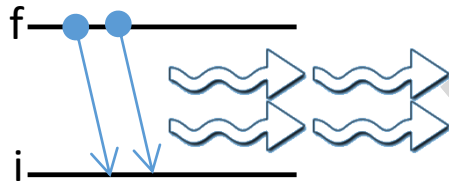
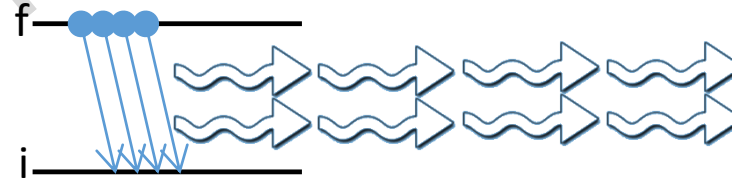
Spectral intensity: A measure of the rate of transfer of energy between matter and electromagnetic field

1. Transition matrix element
2. Density of states at the transition frequency



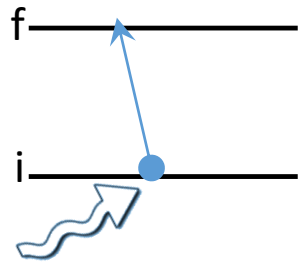
Stimulated Emission

$$P_f(t) = 4V_{fi}^2 \frac{\sin^2 \frac{1}{2} (\omega_{fi} - \omega) t}{(\omega_{fi} - \omega)^2}$$



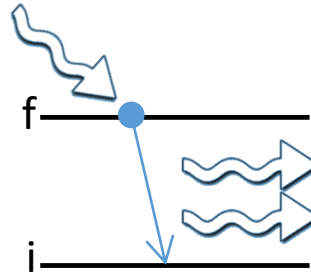
Light Amplification by Stimulated Emission of Radiation

Einstein's Coefficients



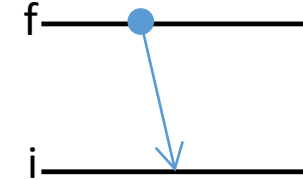
Absorption

$$W_{f \leftarrow i} = B_{if} \rho_{\text{rad}}(E_{fi})$$



Stimulated Emission

$$W_{f \rightarrow i} = B_{fi} \rho_{\text{rad}}(E_{fi})$$



(independent of
energy density of
radiation)

Spontaneous Emission

$$W_{f \rightarrow i}^{\text{spont}} = A_{fi}$$

$$N_i B_{if} \rho_{\text{rad}}(E_{fi}) = N_f (A_{fi} + B_{fi} \rho_{\text{rad}}(E_{fi}))$$

From Boltzmann distribution,

$$\frac{N_f}{N_i} = e^{-E_{fi}/kT}$$

Einstein's Coefficients

$$N_i B_{if} \rho_{\text{rad}}(E_{fi}) = N_f (A_{fi} + B_{fi} \rho_{\text{rad}}(E_{fi}))$$

$$\rho_{\text{rad}}(E_{fi}) = \frac{A_{fi}/B_{fi}}{(B_{if}/B_{fi})e^{E_{fi}/kT} - 1}$$

From Planck distribution
(density of states for EM field),

$$\rho_{\text{rad}}(E_{fi}) = \frac{8\pi h \nu_{fi}^3 / c^3}{e^{E_{fi}/kT} - 1}$$

Relation between Einstein's coefficients

$$B_{fi} = B_{if} \quad A_{fi} = \frac{8\pi h}{c^3} \nu_{fi}^3 B_{fi}$$

From Boltzmann distribution,

$$\frac{N_f}{N_i} = e^{-E_{fi}/kT}$$

- Spontaneous emission outweighs stimulated emission for high energy transitions
- Finite lifetime of excited states due to spontaneous emission

