Lecture 25: Transition Probabilities

Last time: Interaction Picture

$$\hat{H} = \underset{\substack{\uparrow \\ \text{"Free Hamiltonian"}}}{\hat{H}_0} + \hat{H}_{int}(t) \leftarrow \text{usually time dependent}$$

- Operators evolve according to "free Hamiltonian"

$$\hat{A}^{(I)}(t) = \hat{U}_0^\dagger(t)\,\hat{A}^{(I)}(0)\,\hat{U}_0(t)$$

$$\frac{d\hat{U}_0}{dt} = -\frac{i}{\hbar}\hat{H}_0\hat{U}_0 \quad \Rightarrow \quad \hat{U}_0(t) = e^{-\frac{i}{\hbar}\hat{H}_0 t}$$

$$\frac{d}{dt}\hat{A}^{(I)}(t) = -\frac{i}{\hbar}\left[\hat{A}^{(I)}(t), \hat{H}_0(t)\right]$$

- States evolve according to "interaction Hamiltonian"

$$|\Psi^{(I)}(t)\rangle = \hat{U}^{(I)}(t)\,|\Psi^{(I)}(0)\rangle = \hat{U}_0^\dagger(t)\,|\Psi^{(S)}(t)\rangle$$

$$\frac{d\hat{U}^{(I)}}{dt} = -\frac{i}{\hbar}\hat{H}^{(I)}_{int}(t)\,\hat{U}^{(I)}(t), \qquad \hat{H}^{(I)}_{int}(t) = \hat{U}_0^\dagger(t)\,\hat{H}_{int}(t)\,\hat{U}_0(t)$$

Dysan: $$\hat{U}^{(I)}(t) = \underset{\substack{\uparrow \\ \text{time ordered exponential}}}{T}\left\{\exp\left[-\frac{i}{\hbar}\int_0^t \hat{H}^{(I)}_{int}(t')\,dt'\right]\right\}$$

More generally $$\hat{U}^{(I)}(t_f, t_i) = \hat{U}^{(I)}(t_f)\,\hat{U}^{(I)\dagger}(t_i)$$

$$= \hat{U}_0^\dagger(t_f)\,\hat{U}(t_i, t_f)\,\hat{U}_0(t_i)$$

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$$\Rightarrow \hat{U}^{(I)}(t_f, t_i) = T\left\{ \exp\left[-\frac{i}{\hbar}\int_{t_i}^{t_f} \hat{H}^{(I)}_{int}(t')\,dt'\right]\right\}$$

$$= \mathbb{1} - \frac{i}{\hbar}\int_{t_i}^{t_f} \hat{H}^{(I)}_{int}(t')\,dt' + \left(\frac{-i}{\hbar}\right)^2 \int_{t_i}^{t_f} dt' \int_{t_i}^{t'} dt''\, \hat{H}^{(I)}_{int}(t')\,\hat{H}_{int}(t'')$$

$$+ \cdots$$

- Connection to elementary treatment (e.g. Cohen-Tannoudji et al.)

Suppose $\{|u_n\rangle\}$ are the eigenstates of $\hat{H}_0$. They form a complete orthonormal set. The solution (in the <u>Schrödinger</u> picture) for the time evolving state for the full Hamiltonian $\hat{H}(t) = \hat{H}_0 + \hat{H}_{int}(t)$ can be expressed

$$|\Psi^{(S)}(t)\rangle = \sum_n c_n^{(S)}(t)\,|u_n\rangle$$

expansion coefficients in the S-picture

In the interaction picture

$$|\Psi^{(I)}(t)\rangle = \hat{U}_0^{\dagger}(t)\,|\Psi^{(S)}(t)\rangle = \sum_n c_n^{(S)}(t)\,\hat{U}_0^{\dagger}(t)\,|u_n\rangle$$

$$= \sum_n c_n^{(S)}(t)\,e^{+\frac{i}{\hbar}E_n t}\,|u_n\rangle$$

$$= \sum_n c_n^{(I)}(t)\,|u_n\rangle$$

expansion coef in interaction-Pict

$$\Rightarrow c_n^{(S)}(t) = c_n^{(I)}(t)\,e^{-\frac{i}{\hbar}E_n t}$$

$$\Rightarrow \boxed{|\Psi^{(S)}(t)\rangle = \sum_n c_n^{(I)}(t)\,e^{-i\frac{E_n t}{\hbar}}\,|u_n\rangle}$$

Typically, this is an assumed Ansatz

Thus, the expansion coeffs in the interaction picture represent the "part" of the evolution beyond the free $e^{-iE_n t/\hbar}$ for each eigenket.

Transition probabilities

Given state at initial time t_i, $\hat{H}_0$ eigenstate $|u_i\rangle$ what is the probabilities of finding $|u_f\rangle$ after time t?

$$P_{f\leftarrow i} = |\langle u_f|\hat{U}(t_f,t_i)|u_i\rangle|^2 = |\langle u_f|\hat{U}_0^\dagger(t_f)\,\hat{U}^{(I)}(t_f,t_i)\,\hat{U}_0(t_i)|u_i\rangle|^2$$

$$= |\langle u_f|\hat{U}^{(I)}(t_f,t_i)|u_i\rangle|^2$$

Perturbation series:

$$P_{f\leftarrow i} = \Big|\delta_{f\leftarrow i} - \frac{i}{\hbar}\int_{t_i}^{t_f}\langle u_f|\hat{H}_{int}^{(I)}(t')|u_i\rangle\,dt' + $$

$$+\frac{1}{2}\left(-\frac{i}{\hbar}\right)^2\int_{t_i}^{t_f}dt'\int_{t_i}^{t_f}dt''\,\langle u_f|T\{\hat{H}_{int}^{(I)}(t')\,\hat{H}_{in}^{(I)}(t'')\}|u_i\rangle$$

$$+ \cdots \Big| \equiv |C_{f\leftarrow i}^{(0)} + C_{f\leftarrow i}^{(1)} + C_{f\leftarrow i}^{(2)} + \cdots|$$

Each order represents another power of the interaction strength. When the interaction is "weak", we can terminate this in a finite sum. We must be careful to understand when we can do this.

- <u>First order transition amplitude</u>

Assume $|u_f\rangle \neq |u_i\rangle$. Then to lowest order

$$C^{(1)}_{f\leftarrow i} = \frac{-i}{\hbar}\int_{t_i}^{t_f} \langle u_f | \hat{H}^{(I)}_{int}(t') | u_i\rangle \, dt'$$

$$= \frac{-i}{\hbar}\int_{t_i}^{t_f} \langle u_f | \hat{U}_0^{\dagger}(t') \; \hat{H}_{int}(t') \; \hat{U}_0(t') | u_i\rangle \, dt'$$

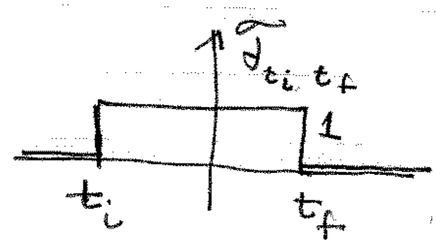
$$= \int_{t_i}^{t_f} e^{i\omega_{fi} t'} \left(\frac{-i}{\hbar} \langle u_f | \hat{H}_{int}(t') | u_i\rangle \right) dt'$$

where $\omega_{fi} \equiv \dfrac{E_f - E_i}{\hbar}$ "Bohr frequency"

$$= \int_{-\infty}^{\infty} dt' \, e^{i\omega_{fi} t'} \; W(t'; t_f, t_i)$$

where $W(t'; t_f - t_i) = \frac{-i}{\hbar} \langle u_f | \hat{H}_{int}(t) | u_i\rangle \; \tilde{\vartheta}(t)$

Time window of perturbation:



$$\Rightarrow \boxed{C^{(1)}_{f\leftarrow i} = \tilde{W}(\omega_{fi}\, ; t_f - t_i) \quad \text{Fourier Transform at } \omega = \omega_{fi}}$$

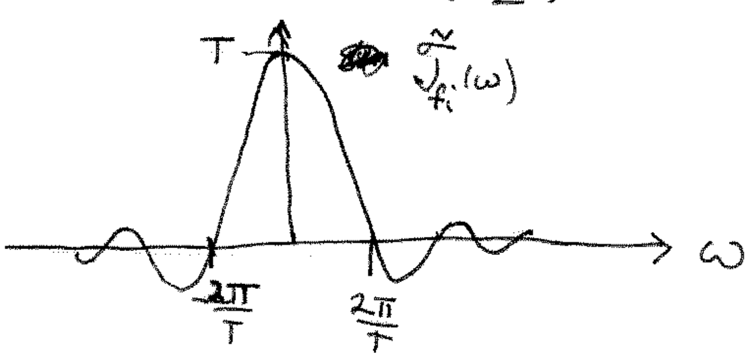
$$\Rightarrow \boxed{c^{(1)}_{f\leftarrow i} = -\frac{i}{\hbar}\, \tilde{H}_{fi}(\omega) \underset{\substack{\Uparrow \\ \text{convolution}}}{\circledast} \tilde{\tilde{J}}_{fi}(\omega)} = \frac{-i}{\hbar}\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\, \tilde{H}_{fi}(\omega-\omega')\, \tilde{\tilde{J}}_{fi}(\omega')$$

where $\tilde{H}_{fi}(\omega) \equiv \int_{-\infty}^{\infty} dt'\, e^{i\omega' t}\, \langle u_f | \hat{H}_{int}(t) | u_i \rangle$

$$\tilde{\tilde{J}}_{fi}(\omega) = \int_{-\infty}^{\infty} dt'\, e^{i\omega t'}\, \tilde{J}_{fi}(t) = \int_{t_i}^{t_f} e^{i\omega t'}\, dt'$$

$$= \frac{e^{i\omega t_f} - e^{i\omega t_i}}{i\omega} = T e^{i\omega T/2} \cdot \frac{e^{i\omega T/2} - e^{-i\omega T/2}}{2i\left(\frac{\omega T}{2}\right)}$$

$$= e^{i\omega T/2}\; T\, \frac{\sin\left(\frac{\omega T}{2}\right)}{\left(\frac{\omega T}{2}\right)} \qquad \text{where } T = t_f - t_i$$



" Diffraction function for single slit "

Note: $\lim_{T\to\infty} \tilde{\tilde{J}}_{fi}(\omega) = 2\pi\, \delta(\omega)\, e^{i\omega T/2}$

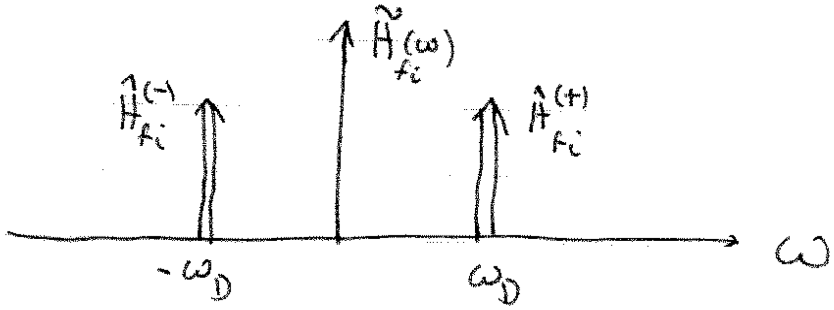
Example: Harmonic Perturbation

$$\hat{H}_{int}(t) = \hat{H}^{(+)}_{int}\, e^{-i\omega_D t} + \hat{H}^{(-)}_{int}\, e^{i\omega_D t}$$

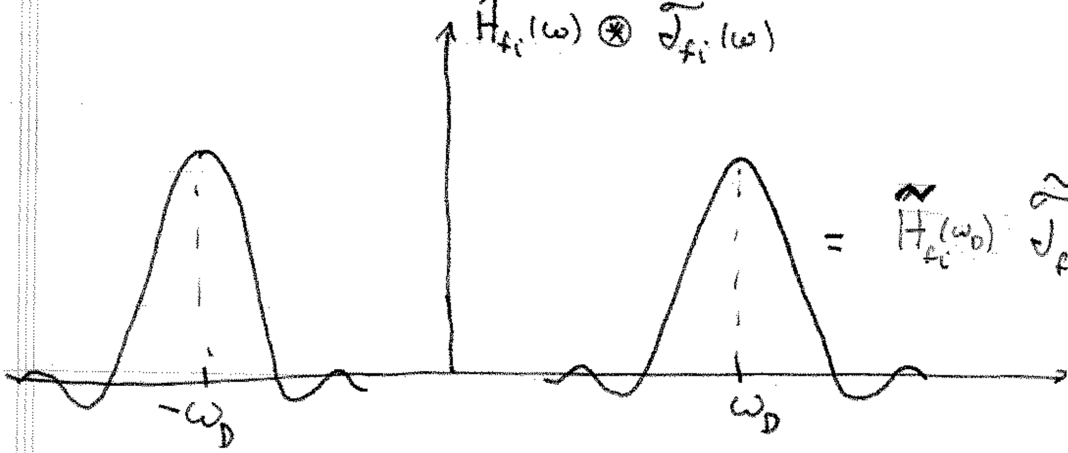
ω_D = driving freq.

$$\rightarrow \tilde{H}_{fi}(\omega) = \int_{-\infty}^{\infty} dt'\, e^{i\omega t'} \langle u_f | \hat{H}_{int}(t') | u_i \rangle$$

$$= \hat{H}^{(+)}_{fi}(\omega_D)\left(2\pi\,\delta(\omega-\omega_D)\right) + \hat{H}^{(-)}_{int}(\omega_D)\left(2\pi\,\delta(\omega+\omega_D)\right)$$



Spikes at $\omega = \pm\omega_D$



$= \tilde{H}_{fi}(\omega_D)\, \tilde{J}_{fi}(\omega-\omega_D)$

Here I have taken $\omega_D \gg \frac{2\pi}{T}$

$$C^{(1)}_{f\leftarrow i} = \frac{-i}{\hbar}\tilde{H}^{(+)}_{fi}(\omega_D)\,\tilde{J}_{fi}(\omega_{fi}-\omega_D) - \frac{i}{\hbar}\hat{H}^{(-)}_{fi}(\omega_D)\,\tilde{J}_{fi}(\omega_{fi}+\omega_D)$$

$$P_{f\leftarrow i} = |C^{(1)}_{f\leftarrow i}|^2$$

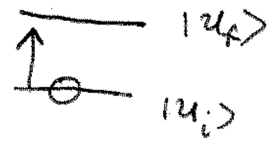
Assuming $\omega_D \gg \frac{2\pi}{T}$, we can ignore cross terms

$$\Rightarrow P_{f\leftarrow i} = \frac{1}{\hbar^2}\left|\tilde{H}^{(+)}_{fi}(\omega_D)\right|^2 \left|\tilde{J}_{fi}(\omega_{fi}-\omega_D)\right|^2 + \frac{1}{\hbar^2}\left|\tilde{H}^{(-)}_{fi}(\omega_D)\right|^2 \left|\tilde{J}_{fi}(\omega_{fi}+\omega_D)\right|^2$$

$$\boxed{P_{fi} = \frac{4\,|\langle u_f|\,\hat{H}^{(+)}_{int}(\omega_D)\,|u_i\rangle|^2}{(E_f - E_i - \hbar\omega_D)^2}\sin^2\left[(\omega_{fi}-\omega_D)\frac{T}{2}\right] + \frac{4\,|\langle u_f|\,\hat{H}^{(-)}_{int}(\omega_D)\,|u_i\rangle|^2}{(E_i - E_f - \hbar\omega_D)^2}\sin^2\left[(\omega_{fi}+\omega_D)\frac{T}{2}\right]}$$

The two terms in the transition probability represent

- Absorption: $E_f > E_i$

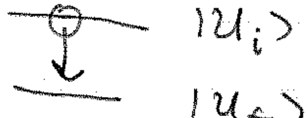


$\Rightarrow E_f > E_i \Rightarrow$ Resonance at $\omega_D = \frac{E_f - E_i}{\hbar}$

$\Rightarrow$ First term dominated

$$P_{f\leftarrow i} = \frac{4\,|\langle u_f|\,\hat{H}^{(+)}(\omega_D)\,|u_i\rangle|^2}{(E_f - E_i - \hbar\omega_D)^2}\sin^2\left[(\omega_{fi}-\omega_D)\frac{T}{2}\right]$$

- Emission: $E_i > E_f$



Second term dominates

$$P_{f\leftarrow i} = \frac{4\,|\langle u_f|\,\hat{H}^{(-)}(\omega_D)\,|u_i\rangle)}{(E_i - E_f - \hbar\omega_D)^2}\sin^2\left[(\omega_{fi}+\omega_D)\frac{T}{2}\right]$$

Validity of the perturbation series and

Perturbation theory requires $P^{(1)}_{f\leftarrow i} \ll 1$

$$\Rightarrow \; |\langle u_f | \hat{H}^{(+)}(\omega_D) | u_i \rangle| \ll |E_f - E_i - \hbar\omega_D|$$

Like time-independent case (with $\omega_D \to 0$; D.C.)

Breaks down on resonance (like degeneracy in T.I.P.T)

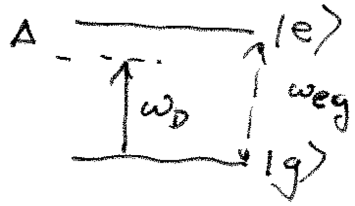
when $E_f - E_i = \hbar\omega_D$

$$P_{f\leftarrow i} = \frac{|\langle u_f | \hat{H}^{(+)}_{int}(\omega_D) | u_i \rangle|^2}{\hbar^2} T^2$$

$\Rightarrow$ In long time limit $\left(T \gg \frac{\hbar}{H_{fi}} \right)$

Our perturbation expansion can break down

Instead, as in degenerate T.I.P.T we can treat the resonant terms independently and solve the problem in this subspace

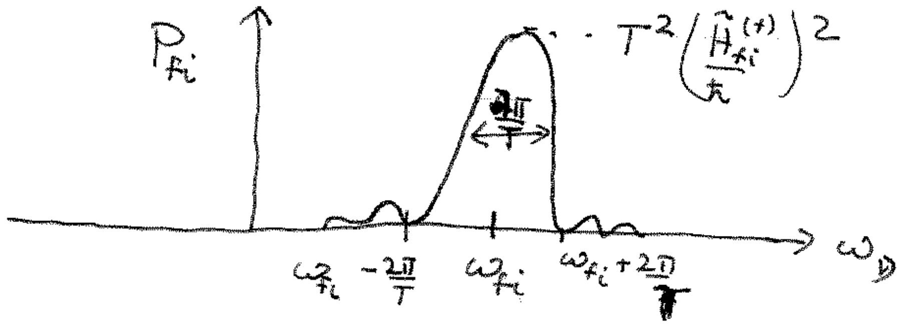


Two levels, resonantly coupled by drive

$\Longrightarrow$ Rabi flopping (next lecture)

Time - energy uncertainty principle

Absorption probability as a function of ω_D



Suppose we want to measure ω_{fi} by measuring P_{fi} as a function of ω_D. We get a "resonance line-shape" like the one above. Our measurement will have an uncertainty $\Delta\omega \sim \frac{2\pi}{T}$, That is, frequencies in the range $\omega_{fi}-\Delta\omega < \omega_D < \omega_{fi}+\Delta\omega$ will have a large $P_{f\leftarrow i}$. Thus we have

$$\Delta\omega\,\Delta t \sim 2\pi \quad \text{or} \quad \boxed{\Delta E\,\Delta t \sim h}$$

This is known as the time-energy uncertainty principle. It is actually quite different from $\Delta x\Delta p \sim h$ which arising from noncommuting observable. "Time" is not an observable, formally.

$\Delta\omega\,\Delta t \sim 2\pi$ is just Fourier duality.

For a finite wave train we do not have monochromatic force $\Rightarrow$ Spectrum of drive is not perfectly narrow

Second order perturbation

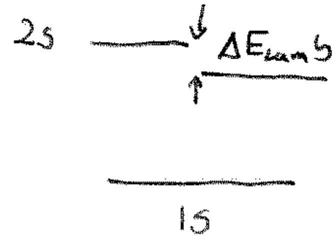
$$c^{(2)}_{f\leftarrow i} = \left(\frac{-i}{\hbar}\right)^2 \int_{t_i}^{t_f} dt' \int_{t_i}^{t'} dt'' \, \langle u_f | \hat{H}^{(I)}_{int}(t') \, \hat{H}^{(I)}_{int}(t'') | u_i \rangle$$

Insert complete: $\sum_m |u_m\rangle\langle u_m| = \hat{1}$

$$= \left(\frac{-i}{\hbar}\right)^2 \sum_m \int_{t_i}^{t_f} dt' \int_{t_i}^{t'} dt'' \, \langle u_f | \hat{H}_{int}(t') | u_m \rangle e^{i\omega_{fm} t'} \langle u_m | \hat{H}_{int}(t'') | u_i \rangle \, e^{i\omega_{fi} t'}$$

The state $|u_m\rangle$ represents an "intermediate" or "virtual" state. We think of the system as making a virtual transition from $|u_i\rangle \to |u_m\rangle$ and then from $|u_m\rangle \to |u_f\rangle$. Note: the virtual state need not conserve energy, but then it is very "short lived" by the time-energy uncertainty relation.

Example: $1s \to 2s$ transition in Hydrogen



$1s \to 2s$ ~~strictly~~ forbidden according to multipole moments
$\Longrightarrow$ First order vanishes

Two-photon transition

- Precision measurement of Q.E.D.
- Connects radio to optical freq.

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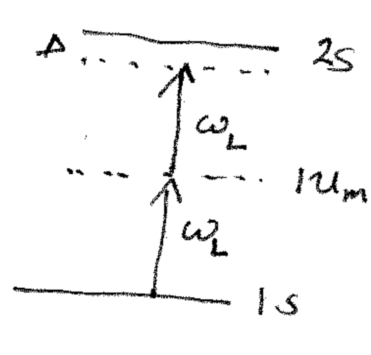


"Virtual state"

e.g. $|2p\rangle$

ω_L = laser freq.

Two absorptions: $\hat{H}_{int}(t) = \hat{H}^{(+)}_{int} e^{-i\omega_L t}$

$$C^{(2)}_{2s\leftarrow 1s} = \left(\frac{-i}{\hbar}\right)^2 \sum_m \tilde{H}^{(+)}_{fm}\, \tilde{H}^{(+)}_{mi} \int_{t_i}^{t_f} dt'\, e^{i(\omega_{fm}-\omega_L)t'} \underbrace{\int_{t_i}^{t'} dt''\, e^{i(\omega_{mi}-\omega_L)t''}}_{\frac{e^{i(\omega_{mi}-\omega_L)t'} - e^{i(\omega_{mi}-\omega_L)t_i}}{i(\omega_{mi}-\omega_L)}}$$

$$= \left(\frac{-i}{\hbar}\right)^2 \sum_m \frac{\tilde{H}^{(+)}_{fm}\, \tilde{H}^{(+)}_{mi}}{i(\omega_{mi}-\omega_L)} \left\{ \int_{t_i}^{t_f} dt' \left[e^{i(\omega_{fi}-2\omega_L)t'}\right] - e^{i(\omega_{mi}-\omega_L)t_i} \int_{t_i}^{t_f} e^{i(\omega_{fm}-\omega_L)t'}\, dt' \right\}$$

Second term is <u>non-resonant</u>

$$\Rightarrow \boxed{C^{(2)}_{2s\leftarrow 1s} \cong \left(\frac{-i}{\hbar}\right) \sum_m \frac{\langle u_f | \hat{H}^{(+)}_{int} | u_m\rangle \langle u_m | \hat{H}^{(+)} | u_i\rangle}{E_m - E_i - \hbar\omega_L} \tilde{\delta}(\omega_{fi} - 2\omega_L)}$$

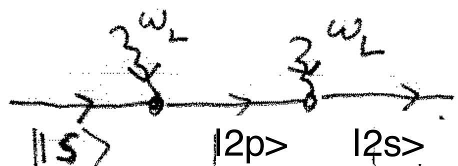
Notes: • Resonance at $\omega_{fi} = 2\omega_L$

• Contributions of virtual states weighted by energy denominator $\frac{1}{E_m - E_i - \hbar\omega_L}$

$\Rightarrow$ time-energy uncertainty

• <u>Feynman diagrams:</u> Graphical representation of perturbation theory

e.g.



each picture $\equiv$ equation

verticies and propagation