GENERAL EXPRESSION FOR RADIATIVE TRANSITION RATES

COUPLED SYSTEM OF RADIATION FIELD AND MATTER (ATOM) IN THE SCHRÖDINGER REPRESENTATION

$$\mathcal{H}\,\Phi(t) = i\hbar \frac{\partial \Phi(t)}{\partial t}$$

TOTAL HAMILTONIAN

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_I$$

INTERACTION BETWEEN MATTER & RADIATION FIELD RESPONSIBLE FOR TRANSITIONS

UNCOUPLED RADIATION AND ELECTRONS

$$\mathcal{H}_0 = \mathcal{H}_E + \mathcal{H}_R$$

$\mathcal{H}_I \equiv \mathcal{H}_{ED}$ IN THE ELECTRIC DIPOLE APPROX.

$$\Phi(t) = \underbrace{\exp\left(i\mathcal{H}(t-t_0)/\hbar\right)}_{\text{TIME-DEVELOPMENT OPERATOR}} \Phi(t_0)$$

KNOWN AT SOME ARBITRARY INSTANT TIME EARLIER MOMENT THAN t

Ψ_f : EIGENSTATE OF $\mathcal{H}_0$

$$\mathcal{H}_0 \Psi_f = \hbar\omega_f \Psi_f$$

THE PROBABILITY THAT THE SYSTEM IS IN STATE Ψ_f AT TIME t

$$|\langle \Psi_f | \Phi(t)\rangle|^2 = |\langle \Psi_f | e^{-i\mathcal{H}(t-t_0)/\hbar} | \Phi(t_0)\rangle|^2$$

$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_I$

BECAUSE OF $\mathcal{H}_I$

$$|\langle \Psi_f | \Phi(t)\rangle|^2 \neq |\langle \Psi_f | \Phi(t_0)\rangle|^2$$

THIS DIFFERENCE IS DUE TO THE RADIATIVE TRANSITIONS DURING THE TIME INTERVAL $[t_0, t]$

THE STATE OF THE COUPLED SYSTEM AT TIME t_0 = LINEAR SUPERPOSITION OF SOLUTIONS OF $\mathcal{H}_0$:

$$\mathcal{H}_0 \Psi_a = \hbar\omega \Psi_u$$

$$\phi(t_0) = \sum_u c_u \Psi_u$$

$$|\langle \Psi_f | \phi(t) \rangle|^2 = \sum_u |c_u(t_0)|^2 \underbrace{|\langle \Psi_f | e^{-i\mathcal{H}(t-t_0)/\hbar} | \Psi_u \rangle|^2}_{\text{PROPORTIONALITY FACTOR}}$$

PROBABILITY THAT THE SYSTEM IS IN THE STATE Ψ_u AT t_0

PROBABILITY THAT THE SYSTEM IS IN THE STATE Ψ_f AT TIME t

TRANSITION RATE FROM STATE Ψ_u TO STATE Ψ_f = TIME DERIVATIVE OF THE PROPORTIONALITY FACTOR

$$f \leftarrow u$$

$$\frac{1}{\tau_f} = \frac{d}{dt} |\langle f | \exp\{-i\mathcal{H}(t-t_0)/\hbar\} | u \rangle|^2$$

INITIAL STATE

$\sum_f$ (FINAL STATES) FOR COMMON EXPERIMENTAL SITUATION

UNDER STEADY-STATES CONDITIONS, τ IS EXPECTED AS INDEPENDENT OF t_0 AND t

HOW TO EVALUATE τ?

EXPANSION IN A SERIES OF POWERS OF THE MATRIX ELEMENTS OF $\mathcal{H}_I$ (THEY ARE SMALL COMPARED WITH THE ENERGIES OF PHOTONS AND ATOMIC TRANSITIONS THEREFORE IT IS EXPECTED THAT THE SERIES IS RAPIDLY CONVERGENT).

SERIES EXPANSION OF $e^{-i\mathcal{H}(t-t_0)/\hbar}$ IN POWERS OF $\mathcal{H}_I$

$$[\mathcal{H}_0, \mathcal{H}_I] \neq 0 \quad , \quad \mathcal{H} = \mathcal{H}_0 + \mathcal{H}_I$$

THEREFORE

$$e^{-i\mathcal{H}t/\hbar} \neq e^{-i\mathcal{H}_0 t/\hbar} \, e^{-i\mathcal{H}_I t/\hbar} \quad !$$

IDENTITY:

$$e^{i\mathcal{H}_0 t/\hbar} \mathcal{H}_I e^{-i\mathcal{H}t/\hbar} = i\hbar \frac{d}{dt}\left[e^{i\mathcal{H}_0 t/\hbar} e^{-i\mathcal{H}t/\hbar}\right]$$

(*) HOMEWORK

INTEGRATION OF BOTH SIDES WITH RESPECT TO t:

$$\int_{t_0}^{t} e^{i\mathcal{H}_0 t_1/\hbar} \mathcal{H}_I e^{-i\mathcal{H}t_1/\hbar} dt_1 = i\hbar \left[e^{i\mathcal{H}_0 t/\hbar} e^{-i\mathcal{H}t/\hbar} - e^{i\mathcal{H}_0 t_0/\hbar} e^{-i\mathcal{H}t_0/\hbar}\right]$$

$$e^{-i\mathcal{H}t/\hbar} = e^{-i\mathcal{H}_0 t/\hbar}\left\{e^{i\mathcal{H}_0 t_0/\hbar} e^{-i\mathcal{H}t_0/\hbar} - \frac{i}{\hbar}\int_{t_0}^{t} e^{i\mathcal{H}_0 t_1/\hbar} \mathcal{H}_I e^{-i\mathcal{H}t_1/\hbar} dt_1\right.$$

IN ORDER TO BE SURE THAT BY THE TIME t (WHEN WE CALCULATE TRANSITION RATE) THE STEADY-STATE CONDITIONS ARE REACHED

$t_0 = -\infty$ AND THE INTERACTION HAS BEEN BUILT SINCE THE DISTANT PAST $(-\infty)$ AND AT TIME t IT REACHES THE FULL STRENGTH

$$\mathcal{H}_I \Rightarrow \mathcal{H}_I e^{\varepsilon t} \qquad \begin{matrix}(\varepsilon \to 0) \\ t_0 \to \infty\end{matrix} \quad \mathcal{H}_I \to 0$$

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_I \Rightarrow \mathcal{H}_0 + \mathcal{H}_I e^{\varepsilon t}$$

AT THE MOMENT t_0 $\quad \mathcal{H} = \mathcal{H}_0 + \mathcal{H}_I \underset{}{e^{\varepsilon t}} \nearrow 0$

$$\mathcal{H} \to \mathcal{H}_0$$

FOR $t = t_0 = -\infty$

$$\circledast \quad \boxed{e^{-i\mathcal{H}t/\hbar} = e^{-i\mathcal{H}_0 t/\hbar}\left\{1 - \frac{i}{\hbar}\int_{-\infty}^{t} e^{i\mathcal{H}_0 t_1/\hbar}\,\mathcal{H}_I\, e^{\varepsilon t_1}\, e^{-i\mathcal{H}t_1/\hbar}\,dt_1\right\}}$$

DEVELOPED AS A POWER SERIES IN $\mathcal{H}_I$ BY ITERATIONS

TIME-DEPENDENT PERTURBATION THEORY

1. ZERO ORDER (IN $\mathcal{H}_I$) CONTRIBUTES TO THE TRANSITION RATE

THE MATRIX ELEMENT

$$\langle f | e^{-i\mathcal{H}t/\hbar} | u\rangle_0 = \langle f | e^{-i\mathcal{H}_0 t/\hbar} | u\rangle = e^{-i\hbar\omega t/\hbar}\langle f | u\rangle = 0$$

$$\begin{cases} \Psi_f \neq \Psi_u \\ \mathcal{H}_0 \Psi_u = \hbar\omega_u \Psi_u \end{cases}$$

2. FIRST ORDER

$$\langle f | e^{-i\mathcal{H}t/\hbar} | u\rangle_1 = -\frac{i}{\hbar}\langle f | e^{-i\mathcal{H}_0 t/\hbar}\int_{-\infty}^{t} e^{i\mathcal{H}_0 t_1/\hbar}\,\mathcal{H}_I\, e^{\varepsilon t_1}\, e^{-i\mathcal{H}_0 t_1/\hbar}\,dt_1 |u\rangle$$

FROM ZERO ORDER

INSTEAD OF $e^{-i\mathcal{H}t_1/\hbar}$

$\mathcal{H}_0 |u\rangle = \hbar\omega_u |u\rangle$

EIGENSTATES OF $\mathcal{H}_0$

$$= -\frac{i}{\hbar} e^{-i\omega_f t}\int_{-\infty}^{t} e^{i\omega_f t_1}\, e^{-i\omega_u t_1}\langle f|\mathcal{H}_I|u\rangle\, e^{\varepsilon t_1}\,dt_1$$

$$= -\frac{i}{\hbar} e^{-i\omega_f t}\,\langle f|\mathcal{H}_I|u\rangle\int_{-\infty}^{t} e^{(i\omega_f - i\omega_u + \varepsilon)t_1}\,dt_1$$

$$= -\frac{i}{\hbar}\langle f|\mathcal{H}_I|u\rangle\,\frac{e^{\varepsilon t - i\omega_u t}}{\omega_u - \omega_f + i\varepsilon}$$

TRANSITION RATE

$$\frac{1}{\tau} = \frac{d}{dt}\sum_f \frac{|\langle f|\mathcal{H}_I|u\rangle|^2}{\hbar^2} \frac{e^{2\varepsilon t}}{(\omega_u-\omega_f)^2+\varepsilon^2}$$

$$= \sum_f \frac{1}{\hbar^2}|\langle f|\mathcal{H}_I|u\rangle|^2 \frac{2\varepsilon e^{2\varepsilon t}}{(\omega_u-\omega_f)^2+\varepsilon^2}$$

$\varepsilon \to 0$ TO PRODUCE SLOW INTRODUCTION OF $\mathcal{H}_I$

$$\frac{1}{\tau} = \left(\sum_f\right)\frac{1}{\hbar^2}|\langle f|\mathcal{H}_I|u\rangle|^2 \lim_{\varepsilon\to 0} \frac{2\varepsilon \underbrace{e^{2\varepsilon t}}_{\to 1}}{(\omega_u-\omega_f)^2+\varepsilon^2}$$

$$\frac{1}{\pi}\lim_{\varepsilon\to 0}\frac{\varepsilon}{(\omega_0-\omega)^2+\varepsilon^2} = \delta(\omega_0-\omega)$$

$$\frac{1}{\tau} = \frac{2\pi}{\hbar^2}\sum_f |\langle f|\mathcal{H}_I|u\rangle|^2\,\delta(\omega_u-\omega_f)$$

FERMI'S GOLDEN RULE

3. SECOND ORDER IN $\mathcal{H}_I$: FIRST ITERATION OF $(*)$

$e^{-i\mathcal{H}t/\hbar}$ IS REPLACED BY THE FIRST ORDER EXPRESSION

$$e^{-i\mathcal{H}t/\hbar} = -\frac{i}{\hbar} e^{-i\mathcal{H}_0 t/\hbar}\int_{-\infty}^{t} e^{i\mathcal{H}_0 t_2/\hbar}\,\mathcal{H}_I\, e^{\varepsilon t_2}\, e^{-i\mathcal{H}_0 t_2/\hbar}\, dt_2$$

$$\Downarrow$$

$$e^{-i\mathcal{H}t/\hbar} = -\frac{i}{\hbar} e^{-i\mathcal{H}_0 t/\hbar}\int_{-\infty}^{t} e^{i\mathcal{H}_0 t_1/\hbar}\,\mathcal{H}_I\, e^{\varepsilon t_1}\left(-\frac{i}{\hbar} e^{-i\mathcal{H}_0 t_2/\hbar}\right.$$

$$\left.\int_{-\infty}^{t_1} e^{i\mathcal{H}_0 t_2/\hbar}\,\mathcal{H}_I\, e^{\varepsilon t_2}\, e^{-i\mathcal{H}_0 t_2/\hbar}\, dt_2\right) dt_1$$

$$\sum_l |l\rangle\langle l| \equiv \mathbb{1}$$

$$= -\frac{1}{\hbar^2} e^{-i\mathcal{H}_0 t/\hbar} \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \, e^{i\mathcal{H}_0 t_1/\hbar} \mathcal{H}_I e^{\varepsilon t_1} e^{-i\mathcal{H}_0(t_1-t_2)/\hbar} \mathcal{H}_I$$

$$e^{\varepsilon t_2} e^{-i\mathcal{H}_0 t_2/\hbar}$$

CONTRIBUTION TO THE TRANSITION RATE AT THE SECOND ORDER

$$\langle f| e^{-i\mathcal{H}t/\hbar} |u\rangle_2 = -\frac{1}{\hbar^2} \sum_l \langle f| e^{-i\mathcal{H}_0 t/\hbar} \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \, \times$$

$$e^{i\mathcal{H}_0 t_1/\hbar} \mathcal{H}_I e^{\varepsilon t_1 - i\mathcal{H}_0(t_1-t_2)/\hbar} |l\rangle\langle l| \mathcal{H}_I e^{\varepsilon t_2} e^{-i\mathcal{H}_0 t_2/\hbar} |u\rangle$$

⋮

TRANSITION RATE CORRECT TO SECOND ORDER IN $\mathcal{H}_I$

$$\frac{1}{\tau} = \frac{2\pi}{\hbar^2} \sum_f \left| \langle f|\mathcal{H}_I|u\rangle + \frac{1}{\hbar} \sum_l \frac{\langle f|\mathcal{H}_I|l\rangle\langle l|\mathcal{H}_I|u\rangle}{\omega_u - \omega_l} \right|^2 \times$$

$$\delta(\omega_u - \omega_f)$$

DIRECT TRANSITION

$f \leftarrow u$

VIRTUAL INTERMEDIATE STATES

ω_l NOT PRESENT IN $\delta(\omega_u - \omega_f)$

CONSERVATION OF ENERGY OF FINAL AND INITIAL STATES

FOR EACH INTERMEDIATE STATE THERE IS AN ENERGY DENOMINATOR THAT REDUCES THE CONTRIBUTION TO THE TRANSITION RATE

⋮

TO THE n-th ORDER:

$$\frac{1}{\tau} = \frac{2\pi}{\hbar^2} \sum_f \left| \langle f|\mathcal{H}_I|u\rangle + \frac{1}{\hbar} \sum_l \frac{\langle f|\mathcal{H}_I|l\rangle\langle l|\mathcal{H}_I|u\rangle}{\omega_u - \omega_l} + \dots \right.$$

$$\left. + \frac{1}{\hbar^{n-1}} \sum_{l_1} \sum_{l_2} \dots \sum_{l_{n-1}} \frac{\langle f|\mathcal{H}_I|l_1\rangle\langle l_1|\mathcal{H}_I|l_2\rangle \dots \langle l_{n-1}|\mathcal{H}_I|u\rangle}{(\omega_u - \omega_{l_1})(\omega_u - \omega_{l_2}) \dots (\omega_u - \omega_{l_{n-1}})} \right|^2 \times$$

$$\delta(\omega_u - \omega_f)$$