(Project deadline extended by 1 day)

Today Instead of V constant in time over the period of application,

we take $V(t) = \underbrace{2v\cos\omega t}_{\text{for } t\geq 0} = v\left(e^{i\omega t} + e^{-i\omega t}\right)$, $\omega > 0$

$$\boxed{\text{General: } P_{n\leftarrow m}(t) = \frac{1}{\hbar^2}\left|\int_0^t \langle\psi_n^0|V(t_1)|\psi_m^0\rangle e^{i\omega_{nm}t_1}\,dt_1\right|^2}$$

$\langle\psi_n^0|V(t_1)|\psi_m^0\rangle = v_{nm}e^{i\omega t_1} + v_{nm}e^{-i\omega t_1}$, $v_{nm} = \langle\psi_n^0|v|\psi_m^0\rangle$

So
$$P_{n\leftarrow m} = \frac{1}{\hbar^2}\left|\int_0^t v_{nm}e^{i\omega t_1}e^{i\omega_{nm}t_1}\,dt_1 + \int_0^t v_{nm}e^{-i\omega t_1}e^{i\omega_{nm}t_1}\,dt_1\right|^2$$

$$= \frac{|v_{nm}|^2}{\hbar^2}\left|\int_0^t e^{i(\omega+\omega_{nm})t_1}\,dt_1 + \int_0^t e^{i(\omega_{nm}-\omega)t_1}\,dt_1\right|^2$$

For W12L1 V constant in time ($\omega = 0$)

$$= \frac{|v_{nm}|^2}{\hbar^2}\left|\frac{e^{i(\omega_{nm}+\omega)t}-1}{\underbrace{\omega_{nm}+\omega}_{\text{1st term}}} + \frac{e^{i(\omega_{nm}-\omega)t}-1}{\underbrace{\omega_{nm}-\omega}_{\text{2nd term}}}\right|^2$$

We introduce the rotating wave approximation (RWA)

Where the driving frequency ω is quite close to the $|\omega_{nm}|$ ($\omega > 0$)

If $\omega_{nm} > 0$, 2nd term dominates

If $\omega_{nm} < 0$, 1st term dominates

denominators are almost zero.

In the RWA, we ignore/drop the non-dominant term.

Take the case $\omega_{nm} > 0$ as an example.

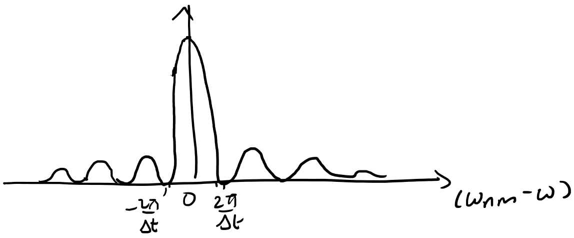
Using the RWA, $P_{n\leftarrow m} = \frac{|v_{nm}|^2}{\hbar^2}\left|\frac{e^{i(\omega_{nm}-\omega)t}-1}{\omega_{nm}-\omega}\right|^2 = \frac{4|v_{nm}|^2}{\hbar^2(\omega_{nm}-\omega)^2}\sin^2\left(\frac{(\omega_{nm}-\omega)t}{2}\right)$

W12L1, $\omega = 0$ $\quad P_{n\leftarrow m} = \frac{|v_{nm}|^2}{\hbar^2}\left|\frac{e^{i\omega_{nm}t}-1}{\omega_{nm}}\right|^2$

$\omega_{nm} \longrightarrow \omega_{nm} - \omega$

Fixed Δt, How does $P_{n\leftarrow m}$ depend on ω_{nm}? (ω is fixed)

$P_{n\leftarrow m}$



$P_{n\leftarrow m}$ is max when

$\omega_{nm} = \omega$ (resonance condition)

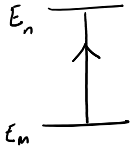
transition freq. ↗ ω_{nm} ; ↖ driving frequency.

$\frac{E_n - E_m}{\hbar}$ (determined by H_0)

Caveat V_{nm} matrix element should be non-zero

↓

selection rules

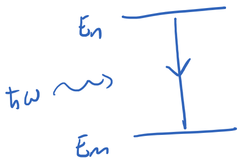


Absorption / Excitation

Intro QM:

$E_n = E_m + \underbrace{\hbar\omega}_{\text{energy of the photon.}}$

$\hat{V}(t) = 2\hat{v}\cos\omega t$ (EM wave ; photons)



stimulated emission / de excitation

(used in lasers)

- Fermi's Golden Rule for constant transition rates

Transition rate = Transition probability per unit time.

not examinable

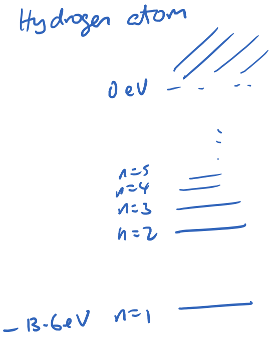
(→ allows to define lifetimes)

Constant transition rate (in time) ⇒ Transition probability ∝ time

Problem Formulation

- Time-dependent perturbation theory
- V is either constant in time or harmonic (within the RWA) ie. close to resonance.
- ★ · Transition from an initial state to a continuum of final states

Eg. Hydrogen atom



} continuum of states

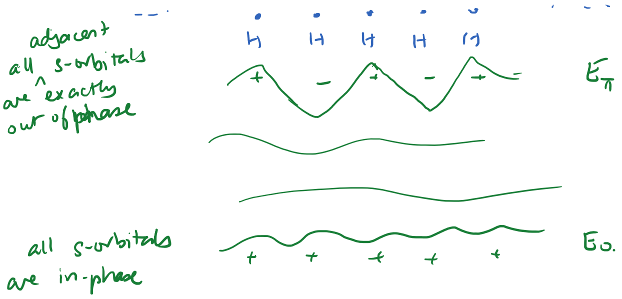
bound states are discrete.

Eg. Solid state physics (condensed phase) – bands.

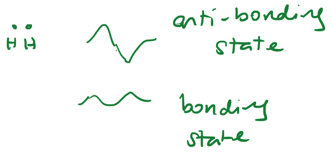
far apart, do not interact

discrete
bound states

Now bring the H atoms, closer together.



earlier H_2 molecule



In between 0 and π, we have other relative phases.
- this results in a continuum of energies between E_0 and E_π.

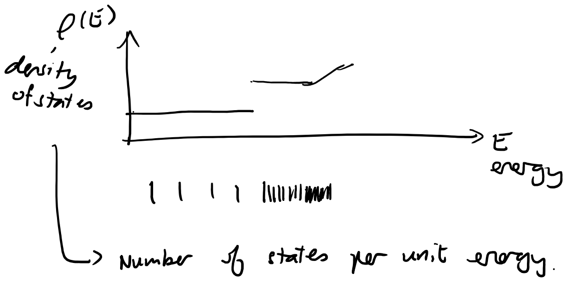
Eg. where we have a continuum of final states
- final state is unbound; or
- final state is a molecular or atomic state coupled to a surface.

(Q) How does having a continuum of final states lead to $P_{\text{trans}} \propto (\Delta t)$ at resonance?

- How do we describe a continuum of states?
  We use the "density of states".

$$\underset{\text{continuum}}{P_{f\leftarrow i}} = \sum_{j=1}^{\text{large}N} P_{f_j\leftarrow i}$$

energy spacing is small



$$= \int \underbrace{\rho(E_f)}_{\text{density of states}} P_{f\leftarrow i}(E_{fi})\, dE_{fi}$$

"weights" for the sum.

Now we work out the transition probability from perturbation theory.

consider $\omega = 0$.

P_{trans} from W12L1

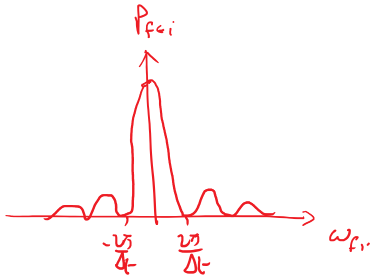
$$\text{Probability} = \int P_{f\leftarrow i}\ \rho(E_f)\, dE_{fi}$$

$$= \int \frac{4|V_{fi}|^2}{\hbar^2} \frac{\sin^2 \frac{\omega_{fi} t}{2}}{\omega_{fi}^2}\ \rho(E_f)\, dE_{fi}$$

no additional approx. so far. *

$$= \int_{-\infty}^{\infty} \frac{4|V_{fi}|^2}{\hbar^2} \frac{\sin^2 \frac{\omega_{fi} t}{2}}{\omega_{fi}^2}\ \rho(E_f)\, dE_{fi}$$

new



new $\quad\quad -\infty$

Approx # 1:

Secondary peaks contribute very little to the integral.

$$= \frac{4|V_{f_0 i}|^2 \rho(E_{f_0})}{\hbar^2} \int_{-\infty}^{\infty} \frac{\sin^2 \frac{\omega_{fi} t}{2}}{\omega_{fi}^2} \, dE_{fi} \qquad \text{where } E_{f_0} = E_i .$$

new

Approx # 2:

middle of primary peak contributes the most and picks up $E_{fi} = 0$, and $|V_{fi}| \rho(E_f)$ is approximately constant over the energy interval $\left(-\frac{2\pi}{\Delta t}, \frac{2\pi}{\Delta t}\right)$

$$= \frac{4}{\hbar^2} |V_{f_0 i}|^2 \rho(E_{f_0}) \int_{-\infty}^{\infty} \frac{\sin^2\left(\frac{E_{fi} t}{2\hbar}\right)}{\left(E_{fi}/\hbar\right)^2} \, dE_{fi} \quad , \quad \omega_{fi} = \frac{E_{fi}}{\hbar}$$

$$\boxed{\int_{-\infty}^{\infty} \frac{\sin^2 u}{u^2} \, du = \pi}$$

Let $u = \frac{E_{fi} t}{2\hbar}$

$du = \frac{t}{2\hbar} dE_{fi}$

$$= 4 |V_{f_0 i}|^2 \rho(E_{f_0}) \int_{-\infty}^{\infty} \frac{\sin^2 u}{\left(\frac{2\hbar}{t}\right)^2 u^2} \left(\frac{2\hbar}{t}\right) du$$

$$= \frac{2}{\hbar} |V_{f_0 i}|^2 \rho(E_{f_0}) \, t \int_{-\infty}^{\infty} \frac{\sin^2 u}{u^2} \, du$$

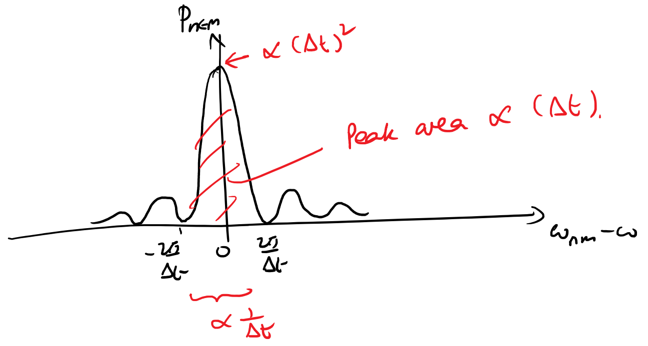
$$= \frac{2\pi}{\hbar} |V_{f_0 i}|^2 \rho(E_{f_0}) \, t \, , \qquad E_{f_0} \approx E_i$$

We see that the probability is proportional to t.

Constant transition rate $= \frac{2\pi}{\hbar} \underbrace{|V_{f_0 i}|^2}_{\langle f_0 | \hat{V} | i \rangle} \rho(E_{f_0})$, $E_{f_0} \approx E_i$, $\omega = 0$.

for $\omega \neq 0$

Constant transition rate $= \frac{2\pi}{\hbar} |V_{f_0 i}|^2 \rho(E_{f_0})$, $E_{f_0} \approx E_i \pm \hbar\omega$, ($\pm$ depends on signs of ω_{fi}, ω)



(essence of Fermi Golden rule)

Now we focus on the matrix element $|V_{nm}|$. which leads to 'selection rules'.

Example: Light-matter interaction.

Recall: Zeeman effect $\quad$ EM wave

$$H = H_0 + \frac{e}{m} \vec{A} \cdot \vec{p}$$

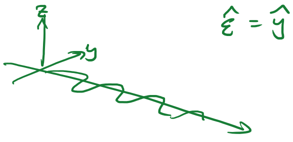
$(q = -e)$ $\quad$ (ignored A^2 term)

Light is an EM wave.

Light $V(t) = \frac{e}{m} \vec{A}(t) \cdot \vec{p}$

$\vec{A} = \underset{\substack{\uparrow \\ \text{denotes the} \\ \text{polarization of} \\ \text{light} \\ \text{(unit vector)}}}{A_0 \hat{\varepsilon}} \cos(\underset{\substack{\uparrow \\ \vec{k}\text{: wave vector.}}}{\vec{k}} \cdot \vec{r} - \omega t)$, $\vec{E} = -\frac{\partial \vec{A}}{\partial t}$

$\hat{\varepsilon} = \hat{y}$



$\vec{k} // \hat{x}$.

$$V(t) = \frac{e}{m} A_0 \cos(\vec{k} \cdot \vec{r} - \omega t) \, \hat{\varepsilon} \cdot \vec{p}$$

$$= \frac{eA_0}{m} \frac{1}{2} \left(e^{i\vec{k} \cdot \vec{r}} e^{-i\omega t} + e^{-i\vec{k} \cdot \vec{r}} e^{i\omega t} \right) \hat{\varepsilon} \cdot \vec{p}$$

So far, no approx.

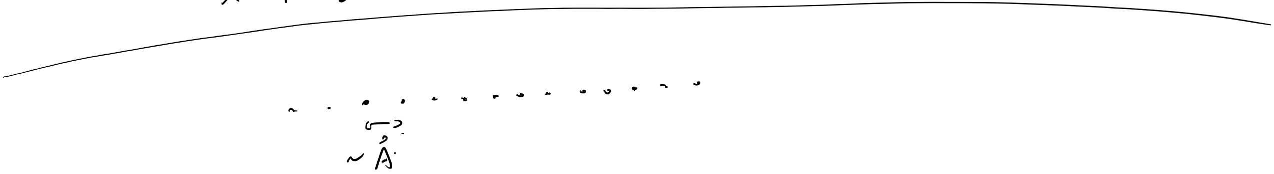
Approx :

$e^{\pm i \vec{k} \cdot \vec{r}} = 1$ ——— called the "dipole approx".

So $V(t) = V(e^{i\omega t} + e^{-i\omega t})$, $V = \frac{eA_0}{2m} \hat{\varepsilon} \cdot \vec{p}$

Why is this mostly valid?

λ of light ~ few hundred nms.



$|\vec{k}| = \frac{2\pi}{\lambda}$. $|\vec{k} \cdot \vec{r}| \approx 0$. , $|\vec{r}| \sim a_0$

$\lambda >> a_0$ Bohr radius.

Approx #2 — RWA.

$$P_{e \leftarrow g}(t) = \frac{4 |V_{eg}|^2}{\hbar^2} \frac{\sin^2((\omega - \omega_{eg})t/2)}{(\omega - \omega_{eg})^2}$$

$$\text{where } |V_{eg}|^2 = \frac{1}{4} \left| \frac{eA_0}{m} \right|^2 |\underbrace{\langle e | \hat{\varepsilon} \cdot \vec{p} | g \rangle}_{\text{momentum matrix elements.}}|^2$$

Can also be written in terms of dipole matrix elements:

$$\langle e | \hat{\varepsilon} \cdot \underbrace{q\vec{r}}_{\text{dipole}} | g \rangle$$

To express V_{eg} in terms of $\vec{r}$ matrix elements, we use:

$$\boxed{\vec{p} = \frac{m}{i\hbar} [\vec{r}, H_0]}$$

$[\vec{r} \quad H]$

To express veg

$$[\vec{r}, H_0]$$
$$= [\vec{r}, \frac{\vec{p}^2}{2m} + \hat{V}(r)]$$
$$= [\vec{r}, \frac{p^2}{2m}]$$
$$= \frac{1}{2m} [\underset{\uparrow \text{vector}}{\vec{r}}, p^2]$$
$$= \frac{1}{2m} (2i\hbar \vec{p})$$
$$= i\hbar \frac{\vec{p}}{m}$$

$$\boxed{\vec{p} = \frac{m}{i\hbar}[\vec{r}, H_0]}$$

valid when potential $\tilde{V}$ for H_0 depends only on r.

$$[\vec{r}, \vec{p}\cdot\vec{p}]_i$$
$$= [r_i, \vec{p}\cdot\vec{p}]$$
$$= [r_i, p_j p_j] \quad \text{(summation notation)}$$
$$= [r_i, p_j]p_j + p_j[r_i, p_j]$$
$$= 2i\hbar \delta_{ij} p_j$$
$$= 2i\hbar p_i$$

momentum matrix element

$$\langle e|\hat{\varepsilon}\cdot\vec{p}|g\rangle = \langle e|\hat{\varepsilon}\cdot\frac{m}{i\hbar}[\vec{r}, H_0]|g\rangle$$
$$= \frac{m}{i\hbar}\langle e|\hat{\varepsilon}\cdot(\vec{r}H_0 - H_0\vec{r})|g\rangle$$
$$= \frac{m}{i\hbar}\langle e|\hat{\varepsilon}\cdot(\vec{r}E_g - E_e\vec{r})|g\rangle$$
$$= \frac{m}{i\hbar}\underbrace{(E_g - E_e)}_{\text{energy term.}}\underbrace{\langle e|\hat{\varepsilon}\cdot\vec{r}|g\rangle}_{\text{position matrix element.}}$$

<u>Next lecture</u> – work out selection rules for the specific case where the states are spherical harmonics.

– adiabatic approx.

<u>Canvas</u> – Past two years' final exam papers.