Appendix A: Time-dependent Perturbation Theory

- Governing equation is TDSE $\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$ (A1)
- Idea:

(i) If $\hat{H} = \hat{H}_0$ (time-independent) and $\hat{H}_0 \psi_n = E_n \psi_n$,

then $\Psi(x,t) = \sum_n a_n \psi_n e^{-iE_n t/\hbar}$ given $\Psi(x,0) = \sum_n a_n \psi_n$

the same (do not depend on time)

(ii) Now $\hat{H} = \hat{H}_0 + \hat{H}'(t)$ (our problem)

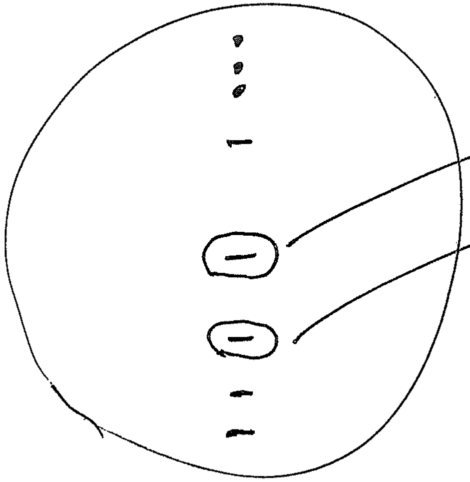
Key idea →

$$\boxed{\Psi(x,t) = \sum_n \underbrace{a_n(t)}_{\text{time dependence must come from } \hat{H}'(t)} \psi_n \underbrace{e^{-iE_n t/\hbar}}_{\text{time evolution due to } \hat{H}_0}} \quad \text{(A2)}$$

Problem is to solve for $a_n(t)$

- Want to get equations for $\frac{d a_n(t)}{dt}$ and solve for $a_n(t)$
- Substitute Eq.(A2) into Eq.(A1) will do the job!

<u>Two-state (two-level) system [make life simpler]</u>



"Atom" ($\hat{H}_0$ problem)

pick two states (any two)

state "2" —— ψ_2, E_2

state "1" —— ψ_1, E_1

$\underbrace{\text{"Atom"}}_{\hat{H}_0 \text{ or } \hat{H}_{atom}}$

Could be:

"1" —— ψ_1, E_1

"2" —— ψ_2, E_2

Initially $(t=0)$, $\left.\begin{array}{l} a_1(0)=1 \\ a_2(0)=0 \end{array}\right\}$ definitely in state "1"

$\boxed{\text{What is } a_2(t) \text{ due to } \hat{H}'(t)\text{?}}$

Could also have picked "7" —— ψ_7, E_7

"3" —— ψ_3, E_3

OR ...

"1" —— ψ_1, E_1 "1" —— ψ_1, E_1

∴ Handling two-level atom first gives result that can be applied to many levels!

- For two-level case, Eq. (A2) reads

effect of $\hat{H}'(t)$ is embedded in the time-dependence in $a_2(t)$ [& $a_1(t)$]

$$\Psi(\vec{r},t) = a_1(t)\underbrace{\psi_1(\vec{r})\,e^{-\frac{iE_1t}{\hbar}}} + a_2(t)\underbrace{\psi_2(\vec{r})\,e^{-\frac{iE_2t}{\hbar}}}$$

$$= a_1(t)\underbrace{\Psi_1(\vec{r},t)}_{\substack{\text{due to } \hat{H}_o \\ \text{(known)}}} + \underbrace{a_2(t)}_{\text{want to get } a_2(t)}\underbrace{\Psi_2(\vec{r},t)}_{\substack{\text{due to } \hat{H}_o \\ \text{(known)}}} \qquad (A2')$$

$$\underbrace{\left(\hat{H}_0 + \hat{H}'\right)\left[a_1(t)\Psi_1(\vec{r},t) + a_2(t)\Psi_2(\vec{r},t)\right]} = \underbrace{i\hbar\frac{\partial}{\partial t}\left[a_1(t)\Psi_1(\vec{r},t) + a_2(t)\Psi_2(\vec{r},t)\right]}$$

$$\cancel{a_1(t)\hat{H}_0\Psi_1(\vec{r},t)} + \cancel{a_2(t)\hat{H}_0\Psi_2(\vec{r},t)} + a_1(t)\hat{H}'\Psi_1(\vec{r},t) + a_2(t)\hat{H}'\Psi_2(\vec{r},t) = \cancel{a_1(t)\,i\hbar\frac{\partial\Psi_1}{\partial t}} + \cancel{a_2(t)\,i\hbar\frac{\partial\Psi_2}{\partial t}} + i\hbar\Psi_1(\vec{r},t)\frac{da_1(t)}{dt} + i\hbar\Psi_2(\vec{r},t)\frac{da_2(t)}{dt}$$

[Because Ψ_1 & Ψ_2 satisfy $\hat{H}_0\Psi_1 = i\hbar\frac{\partial\Psi_1}{\partial t}$ & $\hat{H}_0\Psi_2 = i\hbar\frac{\partial\Psi_2}{\partial t}$]

∴ TDSE gives

$$\boxed{a_1(t)\hat{H}'\Psi_1 + a_2(t)\hat{H}'\Psi_2 = i\hbar\Psi_1\frac{da_1(t)}{dt} + i\hbar\Psi_2\frac{da_2(t)}{dt}} \quad (A3)$$

- Can obtain an equation for $\frac{da_2}{dt}$ (and $\frac{da_1(t)}{dt}$, if needed)
- Left multiply $\Psi_2^*(\vec{r},t)$ and $\int\cdots d^3r$ will give $\frac{da_2(t)}{dt}$ $\left[\Psi_2^*(\vec{r},t) = \psi_2^*(\vec{r})\,e^{iE_2t/\hbar}\right]$

$$a_1(t)\, e^{\frac{i(E_2-E_1)t}{\hbar}} \int \psi_2^*(\vec{r})\,\hat{H}'\,\psi_1(\vec{r})\,d^3r + a_2(t)\int \psi_2^*(\vec{r})\,\hat{H}'\,\psi_2(\vec{r})\,d^3r$$

$$= \quad 0 \quad + \; i\hbar \frac{da_2(t)}{dt}$$

$$\therefore \quad \boxed{i\hbar \frac{da_2(t)}{dt} = a_1(t)\, e^{\frac{i(E_2-E_1)t}{\hbar}} \int \psi_2^*(\vec{r})\,\hat{H}'\,\psi_1(\vec{r})\,d^3r + a_2(t)\int \psi_2^*(\vec{r})\,\hat{H}'\,\psi_2(\vec{r})\,d^3r} \quad (A4)$$

- $\hat{H}' = \hat{H}'(\vec{r},t)$ [e.g. $\hat{H}' = e\vec{r}\cdot\vec{\mathcal{E}}_0 \cos\omega t$; $\hat{H}' = ez\,\mathcal{E}_0\cos\omega t$]
- Can obtain a similar equation for $i\hbar \frac{da_1(t)}{dt}$ (even without work)
- Generalize readily to many-state case [more terms like the 1st term]
- In general, coupled eqs. for $a_1(t)$ & $a_2(t)$ [or more]

- Very humble task – Only want lowest order $a_2(t)$ due to $\hat{H}'$
  - Initial condition: $a_1(0) = 1$, $a_2(0) = 0$
  - Some time t later (with $\hat{H}'$): $a_1(t) \approx 1$, $a_2(t) \ll 1$ (≈ 0)

<u>Meaning</u>: Take Eq.(A4) as

$$\boxed{i\hbar \frac{da_2(t)}{dt} = e^{\frac{i(E_2-E_1)t}{\hbar}} \int \psi_2^*(\vec{r})\, \hat{H}'\, \psi_1(\vec{r})\, d^3r} \qquad (A5)$$

- Key equation (all results follow) [<u>used initial condition</u>]
- Eq.(A5) works for any $\hat{H}'$ & it is 1^{st} order in $\hat{H}'$
- State "2" is arbitrary, could either be $E_2 > E_1$ or $E_2 < E_1$
- Eq.(A5) governs physics of transitions from state 1 to (arbitrary) state 2

"Analyzing" Eq. (A5) : It makes good sense

$$i\hbar \frac{da_2(t)}{dt} = e^{\frac{i(E_2-E_1)t}{\hbar}} \int \psi_2^*(\vec{r}) \underbrace{\hat{H}' \psi_1(\vec{r})} d^3r \qquad \text{(A5)}$$

$\hat{H}_0$ can't take system away from ψ_1, only $\hat{H}'$ can

$\therefore$ $\underbrace{\hat{H}'\psi_1(\vec{r})}$ = Some state that $\hat{H}'$ evolves the system away from ψ_1

some part in ψ_2, some part in ψ_3, etc. [if not two-level system]

Amplitude in ψ_2 = "Project $[\hat{H}'\psi_1(\vec{r})]$ on $\psi_2(\vec{r})$" (inner product)

$$= \int \psi_2^*(\vec{r}) \hat{H}' \psi_1(\vec{r}) d^3r$$

Prefactor $e^{i(E_2-E_1)t/\hbar}$ comes from evolution due to $\hat{H}_0$

has $\vec{r}$ and time dependence

Eq. (A5) $$i\hbar \frac{da_2(t)}{dt} = e^{i(E_2 - E_1)t/\hbar} \int \psi_2^*(\vec{r})\, \hat{H}'\, \psi_1(\vec{r})\, d^3r$$

$$= \int \psi_2^*(\vec{r})\, e^{iE_2 t/\hbar}\, \hat{H}'\, e^{-iE_1 t/\hbar}\, \psi_1(\vec{r})\, d^3r$$

$$\boxed{a_2(t) = \frac{1}{i\hbar} \int_0^t \left[\int \psi_2^*(\vec{r})\, e^{iE_2 t'/\hbar}\, \underbrace{\hat{H}'(\vec{r}, t')}\, e^{-iE_1 t'/\hbar}\, \psi_1(\vec{r})\, d^3r \right] dt'} \quad \text{(A6)}$$

e.g. $\hat{H}'(\vec{r}, t) = e\vec{r} \cdot \vec{\mathcal{E}}_0 \cos\omega t'$

This is Eq. (13) in the notes (Sec. D)

For $\hat{H}'(\vec{r},t) = e\vec{r}\cdot\vec{\mathcal{E}}_0\cos\omega t = -\vec{\mu}\cdot\vec{\mathcal{E}}_0\cos\omega t$,

Eq. (A6) becomes

$$a_2(t) = \frac{1}{i\hbar}\int_0^t \underbrace{\int \psi_2^*(\vec{r})\,\overbrace{[-\vec{\mu}]}^{\text{"}e\vec{r}\text{"}}\,\psi_1(\vec{r})\,d^3r}_{\substack{\text{integration involving}\\ \text{spatial coordinates only}}}\cdot\vec{\mathcal{E}}_0\cos\omega t'\, e^{i(E_2-E_1)t'/\hbar}\,dt'$$

$$= -\left(\int \psi_2^*(\vec{r})\,\vec{\mu}\,\psi_1(\vec{r})\,d^3r\right)\cdot\left(\frac{1}{i\hbar}\vec{\mathcal{E}}_0\int_0^t e^{\frac{i(E_2-E_1)t'}{\hbar}}\cos\omega t'\,dt'\right) \qquad (A7)$$

which is Eq. (14) in Sec. E