Appendix: Time-Dependent Perturbation Theory

- To introduce the key idea
- To arrive at a key equation

The Problem

$$\hat{H} = \underbrace{\hat{H}_0}_{\text{time-independent}} + \underbrace{\hat{H}'(t)}_{\text{time-dependent, usually switched on from some time } t=0} \qquad (A1)$$

knowns: $\hat{H}_0 \psi_n = E_n \psi_n$ (the states of an atom)

Given the atom ($\hat{H}_0$ problem) is in some state initially ($t<0$), how to find the state at time t after $\hat{H}'(t)$ is ON?

Related to transitions: Initially in ψ_n, what is the prob. at time t to find the system (atom) to be in a different state ψ_m?

Motivation

- If $\hat{H}'(t)$ is NOT there, then $\hat{H}_0$ only

Given at time $t=0$, $\Psi(\vec{r},0) = a_1\psi_1 + a_2\psi_2 + \cdots + a_n\psi_n + \cdots$

$$= \sum_n \underbrace{a_n}_{\text{knowns}} \psi_n(\vec{r}) \qquad (A2)$$

then due to $\hat{H}_0$ only same "a_n's"

$$\Psi(\vec{r},t) = \sum_n a_n e^{-iE_n t/\hbar} \psi_n(\vec{r}) \qquad (A3)$$

$[\,|a_n|^2_{(t=0)} = |a_n e^{-iE_n t/\hbar}|^2 \; ; \; \langle H_0\rangle_{t=0} = \langle H_0\rangle_t$ (expectation value)$]$

- But now $\hat{H} = \hat{H}_0 + \hat{H}'(t)$, Eq. (A3) doesn't work any more.

What to do?

Key step: Write $\boxed{\Psi(\vec{r},t) = \sum_n \underbrace{a_n(t)} \psi_n e^{-iE_nt/\hbar}}$ (A4)

- $a_n(t)$ has time-dependence
- $a_n(t)$'s time-dependence must come from $\hat{H}'(t)$
- No approximation yet
- Problem is to find $a_n(t)$'s? Set up $\frac{da_n(t)}{dt}$ eqs.!

Problem becomes an initial value problem

$t=0$: given a_n (or $a_n(0)$), find $a_n(t)$?

[a special case: $a_1 = 1$, all other $a_i = 0$ $(i \neq 1)$, definitely in ψ_1 before $\hat{H}'(t)$ is ON, what will $a_n(t)$ and $|a_n(t)|^2$ be?]

Eq. (A4) is the method called Dirac's method of variation of constants.

(put all $\hat{H}'(t)$ effects into $a_n(t)$)

The governing equation is

$$\hat{H}\Psi = \left(\hat{H}_0 + \hat{H}'(t)\right)\Psi = i\hbar\frac{\partial \Psi}{\partial t} \qquad \text{(A5)}$$

- Substitute Eq. (A4) into LHS and RHS of Eq. (A5), an equation relating $\frac{da_n(t)}{dt}$ results

$$\text{LHS} = \sum_n a_n(t)\underbrace{\hat{H}_0\psi_n}\, e^{-iE_nt/\hbar} + \sum_n a_n(t)\hat{H}'(t)\psi_n e^{-iE_nt/\hbar}$$

$$= \sum_n a_n(t)E_n\psi_n e^{-iE_nt/\hbar} + \sum_n a_n(t)\hat{H}'(t)\psi_n e^{-iE_nt/\hbar}$$

$$\text{RHS} = i\hbar\sum_n a_n(t)\psi_n\left(\frac{-iE_n}{\hbar}\right)e^{-iE_nt/\hbar} + i\hbar\sum_n\frac{da_n(t)}{dt}\psi_n e^{-iE_nt/\hbar}$$

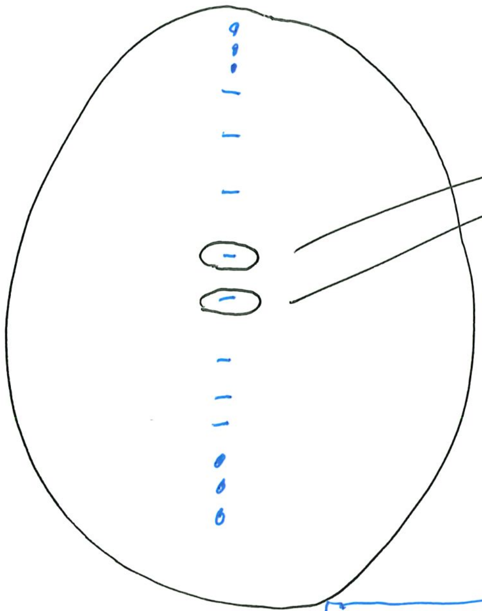
$$= \sum_n a_n(t)E_n\psi_n e^{-iE_nt/\hbar} + i\hbar\sum_n\frac{da_n(t)}{dt}\psi_n e^{-iE_nt/\hbar}$$

(first terms on LHS and RHS cancel)

$\therefore$ TDSE becomes

$$i\hbar \sum_n \frac{da_n(t)}{dt}\, \psi_n e^{-iE_nt/\hbar} = \sum_n a_n(t)\, \hat{H}'(t)\, \psi_n e^{-iE_nt/\hbar} \qquad \text{(A6)}$$

To make it easier to see, consider



pick two states

— state "2" (ψ_2, E_2)

— state "1" (ψ_1, E_1)

Could also be

—— state "1" (ψ_1, E_1)

—— state "2" (ψ_2, E_2)

Consider only <u>two states</u>, Eq. (A6) is:

$$\boxed{i\hbar \frac{da_1(t)}{dt} \psi_1 e^{-iE_1t/\hbar} + i\hbar \frac{da_2(t)}{dt} \psi_2 e^{-iE_2t/\hbar} = a_1(t)\, \hat{H}'(t)\, \psi_1 e^{-iE_1t/\hbar} + a_2(t)\, \hat{H}'(t)\, \psi_2 e^{-iE_2t/\hbar}} \qquad \text{(A7)}$$

Next, extract eqs. for $\frac{da_1}{dt}$ and $\frac{da_2}{dt}$

To isolate the term with $\frac{da_2(t)}{dt}$, left multiply (A7) by $\psi_2^*(\vec{r})$ and $\int\cdots d^3r$

$$i\hbar \frac{da_2(t)}{dt} \underbrace{e^{-iE_2t/\hbar}}_{\text{move it to RHS}} = a_1(t)\, e^{-iE_1t/\hbar} \int \psi_2^*(\vec{r})\, \underbrace{\hat{H}'(t)}_{}\, \psi_1(\vec{r})\, d^3r + a_2(t)\, e^{-iE_2t/\hbar} \int \psi_2^*(\vec{r})\, \hat{H}'(t)\, \psi_2(\vec{r})\, d^3r$$

may have "$\vec{r}$" in $\hat{H}'$ (e.g. $e\vec{r}\cdot\vec{\mathcal{E}}_0 \cos\omega t$)

$$\boxed{i\hbar \frac{da_2(t)}{dt} = a_1(t)\, e^{i(E_2-E_1)t/\hbar} \int \psi_2^*(\vec{r})\, \hat{H}'(t)\, \psi_1(\vec{r})\, d^3r + a_2(t) \int \psi_2^*(\vec{r})\, \hat{H}'(t)\, \psi_2(\vec{r})\, d^3r} \quad (A8a)$$

To isolate $\frac{da_1(t)}{dt}$, left multiply (A7) by $\psi_1^*(\vec{r})$ and $\int\cdots d^3r$

$$\boxed{i\hbar \frac{da_1(t)}{dt} = a_1(t) \int \psi_1^*(\vec{r})\, \hat{H}'(t)\, \psi_1(\vec{r})\, d^3r + a_2(t)\, e^{i(E_1-E_2)t/\hbar} \int \psi_1^*(\vec{r})\, \hat{H}'(t)\, \psi_2(\vec{r})\, d^3r} \quad (A8b)$$

- General so far, Eqs. (A8a) (A8b) $\Leftrightarrow$ Eq. (A7), equivalent to TDSE
- No approximation yet
- Easily generalized to beyond two states
- Haven't applied initial conditions yet

A particularly useful initial condition

$a_1(0) = 1 \quad ; \quad a_2(0) = 0$ before $\hat{H}'(t)$ is ON from $t=0$ onwards

Question: $a_2(t) = ?$ (any chance $|a_2(t)|^2$ of finding system in ψ_2 (state 2))

Lowest (1st) order Approximation

- Initial conditions are also zeroth-order solutions

  when $\hat{H}'(t)$ is NOT there at all!

  $\Psi(\vec{r},0) = 1 \cdot \psi_1(\vec{r}) \quad ; \quad \Psi(\vec{r},t) = 1 \cdot e^{-iE_1t/\hbar}\,\psi_1(\vec{r})$ (if $\hat{H} = \hat{H}_0$)

- Spirit of perturbation

  use zeroth-order solutions in Eq. (A8) [RHS] to get $\frac{da_1(t)}{dt}$ and $\frac{da_2(t)}{dt}$,

  and solve for 1st order solutions $\underbrace{a_2(t)}_{\text{our focus}}$ [and $a_1(t)$]

Applying the idea

- insert $a_1 = 1$ and $a_2 = 0$ on RHS of Eq. (A8a)

Our context: $\hat{H}' = e\vec{r}\cdot\vec{\mathcal{E}}_0 \cos\omega t$

$$i\hbar \frac{da_2(t)}{dt} = e^{i(E_2-E_1)t/\hbar} \int \psi_2^*(\vec{r})\, \hat{H}'(\vec{r},t)\, \psi_1(\vec{r})\, d^3r \qquad (A9)$$

(1st order time-dependent perturbation theory, an eq. governing $\frac{da_2(t)}{dt}$)

$$\boxed{a_2(t) = \frac{1}{i\hbar}\int_0^t e^{i(E_2-E_1)t'/\hbar} \left(\underbrace{\int \psi_2^*(\vec{r})\, \hat{H}'(\vec{r},t')\, \psi_1(\vec{r})\, d^3r}_{\text{over space}} \right) dt'} \qquad (A10)$$

- This is Eq. (13) claimed in class notes (Sec. D)
- Used $\hat{H}'$ is ON from $t=0$ onwards
- Integration constant is zero ($\because a_2(0) = 0$)
- There is a $\underbrace{\text{spatial integral}}_{\text{gives selection rules}}$ and $\underbrace{\text{a temporal integral}}_{\text{gives condition on }\hbar\omega\text{ (as related to }(E_2-E_1))}$

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. (A10) becomes

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

$$= -\left(\int \psi_2^*(\vec{r})\,\vec{\mu}\,\psi_1(\vec{r})\,d^3r\right)\cdot\left(\frac{1}{i\hbar}\vec{\mathcal{E}}_0\int_0^t e^{\frac{i(E_2-E_1)t'}{\hbar}}\cos\omega t'\,dt'\right) \qquad \text{(A11)}$$

which is Eq. (14) in Sec. E and all the physics follows.

How about $a_1(t)$?

- Usually, we don't use the equation because we are interested in transitions
- Apply zeroth-order solutions to Eq. (A8b):

$$\boxed{i\hbar \frac{da_1(t)}{dt} = \int \psi_1^*(\vec{r})\, \hat{H}'(\vec{r},t)\, \psi_1(\vec{r})\, d^3r} \qquad (A12) \qquad \text{(a by-product)}$$

Remarks:

- RHS may be zero (by symmetry argument)
- It contributes a phase to the ψ_1 coefficient in $\Psi(\vec{r},t)$

$$\frac{da_1(t)}{dt} = \frac{1}{i\hbar} H'_{11}(t) \Rightarrow a_1(t) = \frac{-i}{\hbar}\int_0^t H'_{11}(t')dt' + \overset{a_1(0)=1}{\overset{\downarrow}{1}} \approx \underbrace{e^{-\frac{i}{\hbar}\int_0^t H'_{11}(t')dt}}_{\text{just a phase}}$$

$$\therefore\ e^{-\frac{i}{\hbar}\int_0^t H'_{11}(t')dt'}\, e^{-iE_1t/\hbar}\, \psi_1(\vec{r}) \text{ is the term of } \psi_1 \text{ in } \Psi(\vec{r},t)$$

References

For time-dependent perturbation theory, see

- Griffiths, Introduction to Quantum Mechanics
- Bransden and Joachain, Quantum Mechanics

For a more "applied physics" discussion, see

- Yariv, An Introduction to the Theory and Applications of Quantum Mechanics