

A Summer Short Course on Quantum Dynamics & Spectroscopy. (2016)

2016/7/18

Lecture 1: Time-dependent perturbation theory.

- * time-dependent Schrödinger equation.
- * time-evolution operator.
- * pictures of quantum mechanics
- * interaction picture & time-dependent perturbation theory.

⇒ welcome & sign-ups.

⇒ CEIBA & exercises.

This time we will have 8 lectures

to cover time-dependent quantum mechanics

with applications in dynamics & spectroscopy
of condensed-phase molecular systems.

⇒ explain the sequence using CEIBA online timeless

why
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↓

* Why time-dependent quantum mechanics?

- dynamical processes are everywhere ~
- experimental measure "response"

* time-dependent Schrodinger Eq. (TDSE)

Quantum processes are governed by time-dependent Schrodinger equation:

TISE
sets up
to solve
the
"spatial" part
of this
equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = H \cdot |\psi(t)\rangle$$

This equation is a fundamental postulate in quantum mechanics, and there is no need for a proof except for experimental verifications.

Nevertheless, it is instructive to follow a

"deviation" ^{In order to} to understand the basis of the TDSE.

See Sakurai Ch. 2.1 or Tokmakoff ch. 2.

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In QM we like to think that an "operator" drives the time evolution of a wavefunction.

$$\begin{aligned} |\psi(t+\delta t)\rangle &\longrightarrow |\psi(t)\rangle \\ \downarrow &\qquad\qquad\qquad \downarrow \\ \sum_n c_n(t+\delta t) \cdot |\phi_n\rangle &\longrightarrow \sum_n c_n(t) \cdot |\phi_n\rangle \end{aligned}$$

mapping a vector to another vector

Thus, we can define a "time-evolution operator"

$U(t, t_0)$ such that

$$|\psi(t)\rangle = U(t, t_0) \cdot |\psi(t_0)\rangle$$

i.e. U is a matrix, plug into TDSE, we can easily prove the equation of motion for U .

$$i\hbar \frac{\partial}{\partial t} U(t, t_0) = H \cdot U(t, t_0).$$

or, equivalently,

$$U(t, t_0) = U(t_0, t_0) - \int_{t_0}^t d\tau \cdot H(\tau) \cdot U(\tau, t_0)$$

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properties of $U(t, t_0)$.

④

Physically, $U(t, t_0)$ must satisfy the following properties:

① Unitary: wavefunction must be normalized,

$$\text{i.e. } \langle \psi(t_0) | \psi(t_0) \rangle = 1 \quad \text{and} \quad \langle \psi(t) | \psi(t) \rangle = 1.$$

$$\Rightarrow \langle \psi(t) | \psi(t) \rangle = \langle \psi(t_0) | U^\dagger(t, t_0) U(t, t_0) | \psi(t_0) \rangle$$

$$\Rightarrow U^\dagger U = 1 \quad \Rightarrow \quad U^\dagger = U^{-1}$$

② ~~Group~~ Time continuity: $U(t, t) = 1$.

③ Composition property: TDSE is deterministic, therefore

$$U(t_2, t_0) = U(t_2, t_1) U(t_1, t_0) \dots$$

and thus $U(t, t_0) \equiv U(t - t_0)$.
only depends on time difference.

④ time-reversal: $U(t_0, t) U(t, t_0) = 1$.

$$\Rightarrow U^\dagger(t, t_0) = [U(t, t_0)]^\dagger = U(t_0, t) \quad \checkmark$$

timeless

2014
 form for U .
 following

(5)

$$U(t, t_0) = I - \frac{i}{\hbar} \int_{t_0}^t H(\tau) U(\tau, t_0) d\tau.$$

this eq. is recursive and need to be expanded iteratively to yield

$$U(t, t_0) = I + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar}\right)^n \int_{t_0}^t dt_n \int_{t_0}^{t_n} dt_{n-1} \dots \int_{t_0}^{t_2} dt_1 \cdot H(t_n) H(t_{n-1}) \dots H(t_1)$$

if H time-independent

where $t \geq t_n \geq t_{n-1} \dots \geq t_1 \geq t_0$

very often, this is written in an "ordered" time

exponential:

$$U(t, t_0) = \exp_+ \left\{ \frac{-i}{\hbar} \int_{t_0}^t dt \cdot H(t) \right\}.$$

Think \exp_+ as a totally different function

defined by the time-ordered expansion, no need

to relate it to real "exponential",

show this

↳ "unless" → when H is time independent or
 commutes all the time.

timeless

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When H is time-independent or $[H(t_1), H(t_2)] = 0$.

⑥

→ no time-ordering → $U(t, t_0) = e^{-\frac{i}{\hbar} \int_{t_0}^t H(\tau) d\tau}$
= $H_i(t-t_0)$

very often we encounter time-independent Hamiltonian.

then → $U(t, t_0) = e^{-\frac{i}{\hbar} H(t-t_0)}$

Note that functions of operators are defined by their Taylor expansion. In general,

how

$$U(t, t_0) = \exp \left\{ -\frac{i}{\hbar} \int_{t_0}^t H(\tau) d\tau \right\}$$

to
evaluate
this
??

is very difficult to evaluate exactly → needs approximation methods,

next ~~time~~ part we will introduce

how to do that based on the

so-called interaction picture of QM.

So, what is "pictures" of QM?

In the early days of QM, ⁽⁷⁾ ⁽¹⁴⁾ two camps exist and eventually unified by Dirac:

~~Schrodinger~~ Wave mechanics \Rightarrow focus on wave function $\psi(t)$
Matrix mechanics \Rightarrow focus on observable $A(t)$

This reflects on the treatment of quantum dynamics, note that the only physically interesting quantities are observables, i.e., we define a system by the time-dependant observables:

$$\langle \underline{A(t)} \rangle = \langle \psi(t) | A | \psi(t) \rangle = \langle \psi(t_0) | U^\dagger(t, t_0) \cdot A \cdot U(t, t_0) | \psi(t_0) \rangle$$

It is clear that the time dependence can be treated equivalently in two ways:

$\psi(t) \rightarrow |\psi\rangle$ vary in time $\Rightarrow |\psi(t)\rangle = U^\dagger(t, t_0) |\psi(t_0)\rangle$: Schrodinger picture
 $A(t) \rightarrow A$ vary in time $\Rightarrow A(t) = U^\dagger \cdot A \cdot U$: Heisenberg picture, timeless

(8) (12)

* Schrodinger picture : $|\psi(t)\rangle = U(t, t_0) |\psi(t_0)\rangle$

what should be familiar ; \downarrow observable
operator time-independent

wavefunction evolve in time ;

$$\frac{\partial}{\partial t} A = 0$$

$$\frac{\partial}{\partial t} |\psi(t)\rangle = -\frac{i}{\hbar} H |\psi(t)\rangle$$

$$\begin{aligned} \text{observable : } \frac{\partial}{\partial t} \langle A(t) \rangle &= \frac{\partial}{\partial t} \langle \psi(t) | A | \psi(t) \rangle \\ &= -\frac{i}{\hbar} \langle [A, H] \rangle, \end{aligned}$$

* Heisenberg picture : $A_H(t) = U^\dagger(t, t_0) \cdot A_S \cdot U(t, t_0)$

wavefunction time-independent but operator depends on t.

$$\frac{\partial}{\partial t} A_H(t) = \frac{\partial}{\partial t} [U^\dagger(t) A_S U(t)] = -\frac{i}{\hbar} [A_H, H]$$

$$\frac{\partial}{\partial t} |\psi(t)\rangle = 0$$

$$A_S \equiv A_S(t)$$

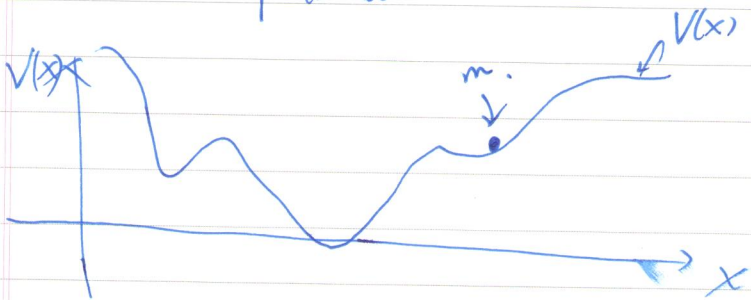
$$\frac{\partial}{\partial t} \langle A(t) \rangle = -\frac{i}{\hbar} \langle [A, H] \rangle$$

timeless

* particle in a potential

⑨ ⑩

Normally ~~in~~ in classes the Heisenberg picture is less frequently mentioned, but it is often very useful to think with a focus on the observables, for example, consider a particle in a potential:



$$\begin{aligned} \hat{x}\hat{p}\hat{p} &= \hbar\hat{p} + \hat{p}\hat{x}\hat{p} \\ &= \hbar\hat{p} + \hbar\hat{p} + \hat{p}\hat{p}\hat{x} \\ &= 2\hbar\hat{p} + \hat{p}\hat{p}\hat{x} \end{aligned}$$

$$\hat{x}\hat{p} = \hbar + \hat{p}\hat{x} \quad \therefore \hat{H} = \frac{\hat{p}^2}{2m} + V(x)$$

EOM for position & momentum operators?

$$\boxed{[\hat{x}, \hat{p}] = i\hbar}$$

$$\Downarrow$$

$$[\hat{x}^n, \hat{p}] = i\hbar n \hat{x}^{n-1}$$

$$[\hat{x}, \hat{p}^n] = i\hbar n \hat{p}^{n-1}$$

$$\dot{\hat{x}}(t) = \frac{-i}{\hbar} [\hat{x}, \hat{H}] = \frac{-i}{\hbar} \left[\hat{x}, \frac{\hat{p}^2}{2m} \right]$$

$$= \frac{-i}{2m\hbar} [\hat{x}, \hat{p}^2] = \frac{-i}{2m\hbar} \{ \hat{x}\hat{p}\hat{p} - \hat{p}\hat{p}\hat{x} \}$$

$$= \frac{-i}{2m\hbar} \{ 2i\hbar\hat{p} + \hat{p}\hat{p}\hat{x} - \hat{p}\hat{p}\hat{x} \} = \frac{\hat{p}}{m}$$

similarly $\dot{\hat{p}}(t) = -\frac{\partial V(x)}{\partial x}$

← exercise

timeless

We see that the equation of motion of the "expectation value" of the particle follows the Newton's equation:

$$m \cdot \frac{d^2}{dt^2} \langle x \rangle = m \frac{d}{dt} \left\langle \frac{dx}{dt} \right\rangle = \frac{d}{dt} \langle p \rangle = - \langle \nabla V \rangle$$

⇒ expectation value of the particle's position & momentum follow classical equation of motion

⇒ Ehrenfest's Theorem.

⇒ Quantum $\xrightarrow{\text{average}}$ classical 

* Interaction pictures

Note that the time-evolution operator provides

us a general way to unify the Schrödinger & the Heisenberg pictures of quantum dynamics.

However, the ^{simple} time-ordered form of $U(t)$ that we have introduced is useless in practice:

$$U(t) = 1 + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar}\right)^n \int_0^t dt_n \int_0^{t_n} dt_{n-1} \dots \int_0^{t_2} dt_1 H(t_n) H(t_{n-1}) \dots H(t_1).$$

⇒ elaborate why this expression is useless.

⇒ H is everything, it converges very slowly!!

For a practical solution to the time-evolution operator, we must consider a

"perturbation picture", i.e., partition the Hamiltonian

timeless

$$H = H_0 + V(t)$$

H_0 : zeroth-order Hamiltonian, ~~so~~ time-independent, which is fully solved \Rightarrow i.e. $U_0(t) = e^{-\frac{i}{\hbar} H_0 t}$ is known.

$V(t)$: perturbation, can be time-dependent. In order for the perturbative approach to be valid, we require $|V(t)| \ll |H_0|$.

Eventually we want to compute the full time evolution operator:

$$U(t) = \exp\left\{ -\frac{i}{\hbar} \int_0^t dt H(t) \right\}$$

total Hamiltonian

But we instead write: $U(t) = U_0(t) \cdot U_I(t)$

the part to be calculated,

should be close to 1 because perturbation is small, timeless

Interaction picture

the part we know

Now the EOM :

$$\text{L.H.S.} \Rightarrow \frac{\partial}{\partial t} U(t) = \frac{-i}{\hbar} H U(t)$$

$$= \frac{-i}{\hbar} (H_0 + V(t)) \cdot U(t)$$

$$\text{R.H.S.} \Rightarrow \frac{\partial}{\partial t} \{ U_0(t) U_I(t) \} = \frac{-i}{\hbar} H_0 \cdot \underbrace{U_0(t) U_I(t)}_{=U(t)} + U_0(t) \cdot \frac{\partial}{\partial t} U_I(t)$$

∴ L.H.S. = R.H.S.

$$\therefore \frac{-i}{\hbar} [H_0 + V(t)] \cdot U(t) = \frac{-i}{\hbar} H_0 U(t) + U_0(t) \cdot \frac{\partial}{\partial t} U_I(t)$$

L.H.S. R.H.S.

We obtaine $\frac{\partial}{\partial t} U_I(t) = \frac{-i}{\hbar} U_0^\dagger(t) \cdot V(t) \cdot U_0(t) \cdot U_I(t)$

$$= \frac{-i}{\hbar} V_I(t) \cdot U_I(t)$$

∴ We defined ^{"time-dependent"} operator " in Interaction picture

$$V_I(t) = U_0^\dagger(t) \cdot V(t) \cdot U_0(t)$$

Now, clearly, $U_I(t)$ is driven by $V_I(t)$, and thus.

$$U_I(t) = 1 + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar}\right)^n \int_0^t dt_n \int_0^{t_n} dt_{n-1} \dots \int_0^{t_2} dt_1 \cdot V_I(t_n) V_I(t_{n-1}) \dots V_I(t_1)$$

Since $V_1(t)$ is the "perturbation" i.e. small quantity,

we can now truncate at a specific "n",

to approximately calculate $U_2(t)$,

For example; up to second order.

receipt
for
calculate
 $U(t)$
perturbatively
!!

$$U_2(t) \approx 1 - \frac{i}{\hbar} \int_0^t dt_1 V_1(t_1) - \frac{1}{\hbar^2} \int_0^t dt_2 \int_0^{t_2} dt_1 V_1(t_2) V_1(t_1)$$

then $U(t) = U_0(t) \cdot U_2(t)$. can be calculated,

In summary, we have:

$$\langle A(t) \rangle = \langle \psi(0) | U^\dagger(t) \cdot A(t) \cdot U(t) | \psi(0) \rangle$$

$$= \langle \psi(0) | U_2^\dagger(t) U_0^\dagger(t) \cdot A(t) \cdot U_0(t) \cdot U_2(t) | \psi(0) \rangle$$

Define $\langle \psi_2(t) |$ wave function & $A_2(t)$ operator, both time-dependent, $| \psi_2(t) \rangle$

In the interaction picture:

Interaction picture

$$H = H_0 + V(t)$$

$$|\psi_I(t)\rangle = U_I(t) \cdot |\psi(0)\rangle$$

FOK

$$A_I(t) = U_0^\dagger(t) \cdot A(0) \cdot U_0(t)$$

$$\therefore \frac{\partial}{\partial t} |\psi_I(t)\rangle = \frac{-i}{\hbar} V_I(t) \cdot |\psi_I(t)\rangle$$

$$\frac{\partial}{\partial t} A_I(t) = \frac{-i}{\hbar} [A_I, H_0]$$

$$\langle A(t) \rangle = \langle \psi_I(t) | A_I(t) | \psi_I(t) \rangle$$

Now both wave functions & operators are time-dependent,

but i) wave function is driven by the perturbation $V_I(t)$,

ii) operator is driven by the zeroth Hamiltonian,

iii) a truncation depends on the smallness of $V(t)$ can be achieved

In the "Interaction Picture" !!

In fact, interaction picture is invented in order to do perturbation !!