A Summer Short Course on Quantum Dynamics & Spectroscopy (2019)

2019/8/13

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.

2014

* Why time-dependent quantum mechanics?

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

⋮

* time-dependent Schrodinger Eq. (TDSE)

Quantum processes are governed by time-dependent schrodinger equation:

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

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

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 "derivation", in order to understand the basis of the TDSE.

See Sakurai Ch. 2.1 or Tokmakoff ch. 2.

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

$$|\psi(t_0)\rangle \longrightarrow |\psi(t)\rangle$$

$$\Downarrow \qquad\qquad \Downarrow$$

$$\sum_n C_n(t_0)\cdot|\phi_n\rangle \longrightarrow \sum_n C_n(t)\cdot|\phi_n\rangle$$

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 proof the equation of motion for U.

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

or, equivalently,

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

2546

* properties of $U(t,t_0)$.

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

① Unitary: wavefunction must be normalized,

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

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

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

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

③ Composition property: TDSE is deterministic, therefore

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

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

④ time-reversal: $U(t_0,t)\,U(t,t_0) = 1$.
$\therefore U^\dagger(t,t_0) = [U(t,t_0)]^{-1} = U(t_0,t)$. ✓

2014

TDM for U.

Following

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

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

$$U(t,t_0) = I + \sum_{n=1}^{\infty}\left(\frac{-i}{\hbar}\right)^n \cdot \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \cdot H(\tau_n) H(\tau_{n-1}) \cdots H(\tau_1)$$

if H time-independent

where $t \geq \tau_n \geq \tau_{n-1} \cdots \geq \tau_1 \geq t_0$

τ_1 to τ_n increasing

very often, this is written in an "time-ordered" exponential:

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

Think $\exp_+$ as a totally differe function defined by the time-ordered expansion, no need to relate it to real "exponential",

show this → "unless" → when H is time independent or commute all the time.

← back to exp. form —

2014

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

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

$= H\,(t-t_0)$.

very often we encounter time-independent Hamiltonian.

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

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

$U(t,t_0) = \exp_{T}\left\{\frac{-i}{\hbar}\int_{t_0}^{t} d\tau\, H(\tau)\right\}$ is very difficult to evaluate exactly $\rightarrow$ needs approximation methods,

how to evaluate this ??

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?

7

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

$\psi(t)$

~~Sch~~ wave mechanics $\Rightarrow$ focus on wave function $\Rightarrow$ Schrödinger picture.

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-dependent observables:

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

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

$\psi(t) \rightarrow$ $|\psi\rangle$ vary in time $\Rightarrow$ $|\psi(t)\rangle = U(t,t_0)|\psi(t_0)\rangle$: Schrödinger pic.

$A(t) \rightarrow$ A vary in time $\Rightarrow$ $A(t) = U^{\dagger} A\, U$: Heisenberg picture.

timeless

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

what should be familiar ; operator time-independency (observable)

wavefunction evolve in time ;

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

,

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

∴ observable : $\frac{\partial}{\partial t}\langle A(t)\rangle = \frac{\partial}{\partial t}\left[\langle\psi(t)|A|\psi(t)\rangle\right]$

$$= \frac{-i}{\hbar}\langle[\hat{A},H]\rangle,$$

* Heisenberg picture ; $A_H(t) = U^{\dagger}(t,t_0)\cdot\hat{A}_S\cdot U(t,t_0)$

wave function time-independency but operator depends on t.

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

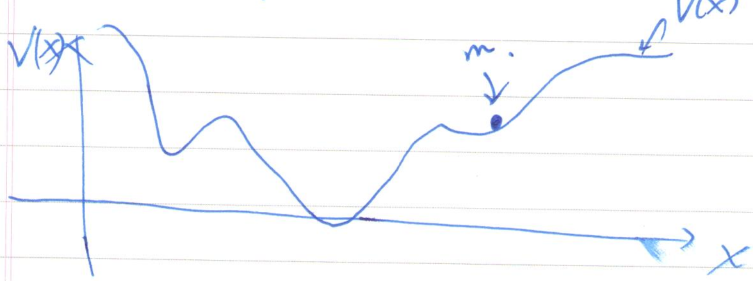
$A_S \equiv A_S(t)$.

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

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

* particle in a potential.

Normally in QM 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:



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

$\hat{x}\hat{p} = i\hbar + \hat{p}\hat{x}$

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

EOM for position & moment operators?

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

$\Downarrow$

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

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

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

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

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

$$m \cdot \frac{\partial^2}{\partial t^2}\langle x \rangle = m \frac{\partial}{\partial t}\left\langle \frac{\partial x}{\partial t} \right\rangle = \frac{\partial}{\partial t}\langle p \rangle$$
$$= -\langle \nabla V \rangle .$$

$\Rightarrow$ expectation value of the particle's position & momentum follow classical equation of motion

$\Rightarrow$ Ehrenfest's Theorem.

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

Set $t_0 = 0$ hereafter

* 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 :

$$U(t) = 1 + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar}\right)^n \int_0^t d\tau_n \int_0^{\tau_n} d\tau_{n-1} \cdots \int_0^{\tau_2} d\tau_1 \, H(\tau_n) H(\tau_{n-1}) \cdots H(\tau_1).$$

⇒) elaborate why this expression is useless.

⇒) $\hat{H}$ is everything, it converged very slowly !!

For a practical solution to the time-evolution operator, we must consider a "perturbation picture", i.e., partition the Hamiltonian

12 14

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

H_0: zeroth-order Hamiltonian, ~~so we~~ time-independent, which is ~~so we~~ 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:

total Hamiltonian

$$U(t) = \exp_+\left\{ \frac{-i}{\hbar}\int_0^t d\tau\, H(\tau) \right\}$$

But we instead write:

the part to be calculated,

$$U(t) = \underline{U_0(t)} \cdot U_I(t)$$

should be close to 1 because perturbation is small.

Interaction picture

the part we know

13 8

Now the EOM :

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

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

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

$\therefore$ L.H.S. = R.H.S.

$$\therefore \underbrace{\frac{-i}{\hbar}[\cancel{H_0} + V(t)] \cdot \overset{U_0(t)\, U_I(t)}{U(t)}}_{LHS} = \underbrace{\cancel{\frac{-i}{\hbar} H_0 \, U(t)} + U_0(t) \cdot \frac{\partial}{\partial t} U_I(t)}_{RHS}$$

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

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

$\therefore$ 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.

$$U_I(t) = 1 + \sum_{n=1}^{\infty} \left(\frac{-i}{\hbar}\right)^n \cdot \int_0^t d\tau_n \int_0^{\tau_n} d\tau_{n-1} \cdots \int_0^{\tau_2} d\tau_1 \cdot V_I(\tau_n) V_I(\tau_{n-1}) \cdots V_I(\tau_1)$$

timeless

Since $V_I(\tau)$ is the "perturbation" i.e. small quantity,
we can now truncate at a specific "n",
to approximately calculate $U_I(t)$,
For example; up to second order.

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

$$U_I(t) \approx 1 - \frac{i}{\hbar}\int_0^t d\tau \cdot V_I(\tau) - \frac{1}{\hbar^2}\int_0^t d\tau_2 \int_0^{\tau_2} d\tau_1 \cdot V_I(\tau_2) V_I(\tau_1)$$

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

In summary, we have:

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

$$= \underbrace{\langle \psi(0)| U_I^{\dagger}(t)}_{\langle \psi_I(t)|} \underbrace{U_0^{\dagger}(t) \cdot A(0) \cdot U_0(t)}_{A_I(t)} \cdot \underbrace{U_I(t) \cdot |\psi(0)\rangle}_{|\psi_I(t)\rangle}$$

Define wave function & operator, both time-dependent,
in the interaction picture:

Interaction picture

TDM

(15)

$$H = H_0 + V(t)$$
$$|\psi_I(t)\rangle = U_I(t) \cdot |\psi(0)\rangle$$
$$A_I(t) = U_0^{\dagger}(t) \cdot A(0) \cdot U_0(t).$$

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

$$\frac{\partial}{\partial t} A_I(t) = \frac{-i}{\hbar}[\hat{A}, H].$$

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

Now both wave functions & operators are time-dependent,

but : ① wave function is driven by the perturbation $V_I(t)$,

② operator is driven by the zeroth Hamiltonian,

③ 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 !!.

timeless