

# Quantum Physics Exercise Class II

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- The state of a quantum state at time  $t$  is totally described by a vector  $|\psi(t)\rangle$  in the Hilbert space  $\mathcal{H}$ .
- The observables correspond to Hermitian operators in  $\mathcal{H}$ . The first quantization condition is given by

$$[\hat{x}, \hat{p}] = i\hbar. \quad (1)$$

- The eigenvalues of an observable  $\hat{A}$  determine the possible results of measuring  $A$ . The probability of obtaining  $a_n$  is given by

$$\mathbb{P}(|\psi\rangle \rightarrow |a_n\rangle) = |\langle\psi|a_n\rangle|^2. \quad (2)$$

After the measurement, the system will collapse to the eigenstate  $|a_n\rangle$ .

- Time evolution is determined via the Schrödinger equation

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle. \quad (3)$$

- Particles are classified as *Bosons* and *Fermions*.

Note:

- For a mixed state, the system is described by the density operator,

$$\hat{\rho}(t) \equiv \sum_j p_j |\psi_j(t)\rangle \langle \psi_j(t)|, \quad (4)$$

where  $p_j$  is the probability of the system being in the state  $|\psi_j(t)\rangle$ .

- For the system described by the generalized coordinates  $q_i$  and momenta  $p_i$ , one can construct the observables as  $A(q, p) \rightarrow \hat{A}(\hat{q}, \hat{p}) \equiv \hat{A}^\dagger(\hat{q}, \hat{p})$ , with the canonical quantization condition satisfying.
- Bosons are particles with integer spin and the total wave function symmetric with respect to the exchange of two particles, while fermions are particles with half-integer spin and the total wave function antisymmetric. The commutation relations of spin operators are given by

$$[\hat{S}_i, \hat{S}_j] = i\hbar \epsilon_{ijk} \hat{S}_k. \quad (5)$$

- The density operator is a Hermitian operator, and it satisfies  $\text{Tr}\hat{\rho} = 1$  and

$$\text{Tr}\hat{\rho}^2 \leq \text{Tr}\hat{\rho}, \quad (6)$$

where the equality holds iff  $\hat{\rho}$  is a pure state.

- The introduction of the density operator is due to our innocence of the total system's information.
- A truly isolate system is described by a pure state. But if we focus on a subpart of the isolate total system, the state of the subsystem is described by a mixed state. Specifically, the reduced density operator,

$$\rho_{\text{sub}}(x, x') \equiv \int dq \Psi^*(x, q)\Psi(x', q) \quad (7)$$

is a mixed state. The above equation can be recast as

$$\hat{\rho}_{\text{sub}} = \text{tr}_{\text{env}}(|\Psi\rangle\langle\Psi|). \quad (8)$$

Possible questions:

- Measurement vs. Time evolution
- Why do we need boson and fermion?

- Propagator:  $|\psi(t)\rangle \equiv U(t, t_0)|\psi(t_0)\rangle$ .
- Equation of propagator:

$$\frac{\partial}{\partial t}U(t, t_0) = -iH(t)U(t, t_0). \quad (9)$$

- Formal solution:

$$U(t, t_0) = T_+ \exp \left[ -i \int_{t_0}^t d\tau H(\tau) \right]. \quad (10)$$

- If  $H$  is independent of time, then  $U(t, t_0) \equiv G(t - t_0) = e^{-iH(t-t_0)}$ .
- If  $\forall t, t', [H(t), H(t')] = 0$ , then  $U(t, t_0) \equiv e^{-i \int_{t_0}^t d\tau H(\tau)}$ .
- Isomorphically, for density matrix, we have

$$\rho(t) = \mathcal{U}(t, t_0)\rho(t_0) \quad (11)$$

with

$$\frac{\partial}{\partial t}\mathcal{U}(t, t_0) = -i\mathcal{L}(t)\mathcal{U}(t, t_0). \quad (12)$$

Here  $\mathcal{L}(t)(\cdot) \equiv [H(t), (\cdot)]$ .

- Schrödinger picture:  $\rho(t_0) \rightarrow \rho(t)$ ,  $\hat{A} \rightarrow \hat{A}$ ;
- Heisenberg picture:  $\rho(t_0) \rightarrow \rho(t_0)$ ,  $\hat{A} \rightarrow \hat{A}(t) = U^\dagger(t, t_0)\hat{A}U(t, t_0)$  and

$$\dot{\hat{A}}(t) = -i[\hat{A}(t), H(t)]. \quad (13)$$

- Interaction picture (Dirac picture):  $\rho(t_0) \rightarrow \rho_I(t) = U_I(t, t_0)\rho(t_0)U_I^\dagger(t, t_0)$ ,  $\hat{A}_I(t) \equiv U^\dagger(t, t_0)\hat{A}(t)U(t, t_0)$ .

Note that: no matter what picture you take, the average of one observable remains the same.

However, different picture has different convenience. For example,

$$\langle \hat{A}(t_1)\hat{B}(t_2) \rangle = \text{Tr}[U^\dagger(t_1, t_0)\hat{A}U(t_1, t_0)U^\dagger(t_2, t_0)\hat{B}U(t_2, t_0)\rho(t_0)]. \quad (14)$$

How to express it in the Schrödinger picture?

Consider the Liouville–von Neumann equation

$$\dot{\rho}(t) = -i[H, \rho(t)], \quad (15)$$

then the steady state is given by

$$\rho^{\text{st}} \equiv \rho(\infty) \quad (16)$$

satisfying

$$\dot{\rho}^{\text{st}} = [H, \rho^{\text{st}}] = 0. \quad (17)$$

With respect to the steady state, we have

$$\langle \hat{A}(t) \rangle = \langle \hat{A} \rangle, \quad (18)$$

$$\langle \hat{A}(t) \hat{B}(t_0) \rangle = \langle \hat{A}(t - t_0) \hat{B} \rangle. \quad (19)$$

The steady state can take the form of

$$\rho^{\text{st}} = \rho^{\text{st}}(H). \quad (20)$$

For example, the density operator for a canonical ensemble is given by

$$\rho^{\text{eq}} = \frac{e^{-\beta H}}{\text{Tr} e^{-\beta H}} = \rho^{\text{eq}}(H). \quad (21)$$



The partition function is defined by

$$Z \equiv \text{Tr} e^{-\beta H} = \sum_n e^{-\beta E_n}. \quad (22)$$

Therefore the energy average is given by

$$\langle H \rangle = \sum_n E_n e^{-\beta E_n} / Z = -\frac{\partial}{\partial \beta} \ln Z. \quad (23)$$

If the Hamiltonian satisfies

$$H|n\rangle = \omega(n + 1/2)|n\rangle \quad (24)$$

with  $n \in \mathbb{N}^+$ ,

$$Z = \sum_n e^{-\beta\omega/2} e^{-n\beta\omega} = \frac{e^{-\beta\omega/2}}{1 - e^{-\beta\omega}} = \frac{1}{2 \sinh(\beta\omega/2)}. \quad (25)$$

## Solve the Schrödinger equation numerically

In matrix form, the Schrödinger equation can be recast into

$$\frac{d}{dt} \begin{bmatrix} c_1(t) \\ c_2(t) \\ \vdots \end{bmatrix} = -i\mathbf{H}(t) \begin{bmatrix} c_1(t) \\ c_2(t) \\ \vdots \end{bmatrix}. \quad (26)$$

Or the Liouville–von Neumann equation,

$$\frac{d}{dt} \begin{bmatrix} \rho_{11} & \rho_{12} & \cdots & \rho_{1n} \\ \rho_{21} & \rho_{22} & \cdots & \rho_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ \rho_{n1} & \rho_{n2} & \cdots & \rho_{nn} \end{bmatrix} = -i\mathbf{H}(t)(\rho)_{mn} + i(\rho)_{mn}\mathbf{H}(t). \quad (27)$$

To solve them, you can use the methods you learn in the computational mathematics. The most prevalent algorithm is the Runge–Kutta 4 (RK4).

But how to solve equations expressed by momenta and coordinates?

Consider the Hamiltonian

$$H = \frac{\hat{p}^2}{2m} + V(\hat{x}) \equiv T + V. \quad (28)$$

We have

$$e^{-iH\Delta t} = e^{-iV\Delta t/2} e^{-iT\Delta t} e^{-iV\Delta t/2} + \mathcal{O}(\Delta t^3). \quad (29)$$

Then

$$e^{-iHt} = \lim_{N \rightarrow \infty} [e^{-iH\Delta t}]^N = \lim_{N \rightarrow \infty} \left[ e^{-iV\Delta t/2} e^{-iT\Delta t} e^{-iV\Delta t/2} \right]^N \quad (30)$$

with  $\Delta t \equiv t/N$ .

Given  $\Psi(x, 0) \equiv \langle x | \Psi(t = 0) \rangle$ , we have

$$\begin{aligned}
 \Psi(x, \Delta t) &= \langle x | e^{-iH\Delta t} | \Psi(0) \rangle \\
 &= \int dx' \int dp \int dx'' \langle x | e^{-iV\Delta t/2} | x' \rangle \langle x' | e^{-iT\Delta t} | p \rangle \langle p | e^{-iV\Delta t/2} | x'' \rangle \langle x'' | \Psi(0) \rangle \\
 &= \frac{1}{2\pi} \int dp \int dx'' e^{-iV(x)\Delta t/2} e^{-ip^2\Delta t/(2m)} e^{ipx} e^{-iV(x'')\Delta t/2} e^{-ipx''} \Psi(x'', 0) \\
 &= e^{-iV(x)\Delta t/2} \mathcal{F}^{-1} [ e^{-ip^2\Delta t/(2m)} \mathcal{F} [ e^{-iV(x'')\Delta t/2} \Psi(x'', 0) ] ]
 \end{aligned} \tag{31}$$

Do the iteration step by step, and you can obtain  $\Psi(x, t)$ . Here the Fourier transformation can be realized via the Fast Fourier Transformation algorithm (FFT), that is

$$\tilde{x}_k = \sum_{n=0}^{N-1} x_n e^{-i2\pi kn/N}, \tag{32}$$

$$x_n = \frac{1}{N} \sum_{k=0}^{N-1} \tilde{x}_k e^{i2\pi kn/N}. \tag{33}$$

Open question: The canonical quantization is based on the Hamilton mechanics, and how can we quantize the system via the Lagrange?

- Main result (R. Feynman in his PhD thesis):

$$\langle q|e^{-iH(t-t_0)}|q_0\rangle = \int_{q(t_0)=q_0}^{q(t)=q} \mathcal{D}[q(t)] e^{iS[q(t)]}, \quad (34)$$

where the functional integral is defined via

$$\int \mathcal{D}q \equiv \lim_{\Delta t \rightarrow 0} \prod_j \int \prod_a dq_a^j [\det(2\pi i \mathbf{A})]^{-1/2}, \quad (35)$$

being the summation of all the possible paths from  $q_0$  to  $q$  and the action is given by

$$S[q(t)] = \int_{t_0}^t dt L[q, \dot{q}], \quad (36)$$

with

$$L[q, \dot{q}] \equiv \sum_a p_a \dot{q}_a - H[p, q] \quad (37)$$

and

$$H[p, q] = \frac{1}{2} \sum_{ab} A_{ab}(q) p_a p_b + \sum_a B_a(q) p_a + C(q). \quad (38)$$

- The classical path is given by

$$\delta S[q(t)] = 0 \quad \Rightarrow \quad \frac{\partial L}{\partial q_\alpha} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_\alpha} = 0. \quad (39)$$

in the limit of  $\hbar \rightarrow 0$ .

- The quantum effect can be viewed as fluctuations around the classical path.
- From the Lagrangian, one can easily analyze the symmetry of the system, that is, obtaining the conserved quantities based on the Noether's theorem.
- Path integral is widely used in the quantum field theory as a useful tool to perform the perturbation expansion.
- Recent some chemical dynamics theories utilize the path integral formalism to study the quantum effect in the chemical reactions by only performing classical evolutions.

To be...