Lecture 4: Equations of motion and canonical quantization

Read Sakurai Chapter 1.6 and 1.7

In Lecture 1 and 2, we have discussed how to represent the state of a quantum mechanical system based the superposition principle and statistical interpretation. Now we need to solve the problem of the time evolution of quantum mechanical states.

1 Equation of motion: the Schrödinger equation

Time-evolution operator We start with the time evolution of a pure state. Suppose that at time t_0, the state is $|\Psi(t_0)\rangle$. Let it evolve to time t, the state becomes $|\Psi(t)\rangle$. We define the time evolution operator $T(t,t_0)$ which is determined by the system, say, the mass of particles and interactions among them. But $T(t,t_0)$ does not depend on which state it applies. Before we derive the concrete form of $T(t,t_0)$, we should be able to conclude that it satisfies the following properties.

1. $T(t,t_0)$ should be a linear operator as required by the superposition principle, *i.e.*,

$$T(t,t_0)(c_1|\Psi_1(t_0)\rangle + c_2|\Psi_2(t_0)\rangle) = c_1T(t,t_0)|\Psi_1(t_0)\rangle + c_2T(t,t_0)|\Psi_2(t_0)\rangle. \quad (1)$$

2. $T(t_0,t_0) = 1$.

3. $T(t_2,t_0) = T(t_2,t_1)T(t_1,t_0) = 1$.

4. $T(t_0,t_1)T(t_1,t_0) = T(t_1,t_0)T(t_0,t_1) = 1$, or $T^{-1}(t_0,t_1) = T(t_1,t_0)$.

5. Once $|\Psi(t_0)\rangle$ is normalized, *i.e.*, $\langle\Psi(t_0)|\Psi(t_0)\rangle = 1$, then at time t, $|\Psi(t)\rangle$ should also be normalized, *i.e.*, $\langle\Psi(t)|\Psi(t)\rangle = 1$. Thus T should be a unitary operator $T^\dagger(t_1,t_0)T(t_1,t_0) = 1$. From 4. and 5, we have

$$T^\dagger(t,t_0) = T(t_0,t). \quad (2)$$

6. For two independent systems A and B, the state vectors can be written as a tensor product $|\phi_A(t)\rangle \otimes |\phi_B(t)\rangle$, the total time evolution operator $T_{AB}(t_1,t_0) = T_A(t_1,t_0) \otimes T_B(t_1,t_0)$.

Equations of motion We can write down equations of motion of state vectors based on the infinitesimal generator of T. Let us take the first order time derivative of $|\Psi(t)\rangle$ as

$$\frac{\partial\Psi(t)}{\partial t} = \lim_{t^{\prime}\to t}\frac{\Psi(t^{\prime}) - \Psi(t)}{t^{\prime} - t} = \lim_{t^{\prime}\to t}\frac{T(t^{\prime},t) - 1}{t^{\prime} - t}\Psi(t) = \frac{\partial T(t^{\prime},t)}{\partial t^{\prime}}|_{t^{\prime}=t}\Psi(t). \quad (3)$$

Next we prove that $\frac{\partial T(t^{'},t)}{\partial t^{'}}|_{t^{'}=t}$ is an anti-Hermitian operator. From $T^{\dagger}(t^{'},t)T(t^{'},t)=1$, we have

$$\frac{\partial T^{\dagger}(t^{'},t)}{\partial t^{'}}T(t^{'},t)+T^{\dagger}(t^{'},t)\frac{\partial T(t^{'},t)}{\partial t^{'}}=0. \tag{4}$$

Set $t^{'}\to t$, we have

$$\frac{\partial T^{\dagger}(t^{'},t)}{\partial t^{'}}|_{t^{'}=t}+\frac{\partial T(t^{'},t)}{\partial t^{'}}|_{t^{'}=t}=0. \tag{5}$$

We set $\hat{M}(t)\equiv i\partial T(t^{'},t)/\partial t^{'}|_{t^{'}=t}$, then $\hat{M}(t)$ is a Hermitian operator and

$$i\frac{\partial}{\partial t}|\Psi(t)\rangle=\hat{M}(t)|\Psi(t)\rangle. \tag{6}$$

$\hat{M}(t)$ should be a linear operator as required by superposition principle, and its Hermiticity comes from the unitarity of time evolution operator. $\hat{M}(t)$ is also additive, i.e. for two independent systems A and B, we should have $\hat{M}_{AB}(t)=\hat{M}_A(t)+\hat{M}_B(t)$.

Then what is $\hat{M}$?

Why Hamiltonian? Consider an infinitesimal time interval Δt, and expand $|\Psi(t-\Delta t\rangle=|\Psi(t)\rangle+i\Delta t\hat{M}(t)|\Psi(t)\rangle$, then

$$\langle\Psi(t-\Delta t)|\Psi(t)\rangle-\langle\Psi(t)|\Psi(t)\rangle\sim i\Delta t\langle\Psi(t)|\hat{M}(t)|\Psi(t)\rangle. \tag{7}$$

Consider a time-translation invariant system, and take the limit $\Delta t\to 0$, we have

$$\lim_{\Delta t\to 0}\frac{\langle\Psi(t-\Delta t)|\Psi(t)\rangle-\langle\Psi(t)|\Psi(t)\rangle}{\Delta t}=\langle\Psi(t)|i\hat{M}(t)|\Psi(t)\rangle. \tag{8}$$

The left-hand-side is independent of t because time-translation symmetry, thus $\langle\Psi(t)|i\hat{M}(t)|\Psi(t)\rangle$ should be a conserved quantity. Such a conserved quantity originates from the time translation symmetry, and it is also additive. In classic theory, it is nothing but Hamiltonian up to a constant, and we denote this constant as $\hbar$, i.e., $\hbar\hat{M}=\hat{H}$. Now we have the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle=\hat{H}|\Psi(t)\rangle. \tag{9}$$

2 Canonical quantization

Still, we need to determine the operator of Hamiltonian. Actually, every quantum theory originates from a classic theory. The process from classic theory to quantum theory is called quantization. A common method is the so-called canonical quantization with the following steps. The process of canonical quantization ensures that quantum mechanical equations of motions have a classic correspondence.

1. (Classic mechanics) Determine the classic Hamiltonian and classic mechanical observables as functions of a set of fundamental observables. Usually, the fundamental observables are chosen as canonical coordinates and momenta.

2. (Canonical quantization condition) Determine the operators of the fundamental observables. The relation between operators of canonical coordinates and momenta are called quantization condition.

3. (QM) Assume the relations between operators of observables and the fundamental operators in quantum mechanics are the same as those in classical mechanics by the spirit of the correspondence principle.

3 Operators of momenta of the Cartesian coordinates

We have derived before that the operator of coordinate in the coordinate representation is just the coordinate itself. Now we need to derive the operator for momentum.

We start from the translation operator $U(\vec{R})$ under the spatial translation $\vec{R}$. In classic mechanics, the coordinate and momentum transform as

$$(\vec{r},\vec{p}) \longrightarrow (\vec{r}+\vec{R},\vec{p}). \tag{10}$$

In quantum mechanics, for a state vector $|\Psi\rangle$, we denote that after such a translation,

$$|\Psi^R\rangle = U(\vec{R})|\Psi\rangle. \tag{11}$$

For two successive translations $\vec{R}_1$ and $\vec{R}_2$, their total effect is equivalent to a new translation $\vec{R}_3 = \vec{R}_1 + \vec{R}_2$. At current stage, we only consider the case without magnetic field, such that any two translations commute. We require that U satisfies

$$U(\vec{R}_3) = U(\vec{R}_1)U(\vec{R}_2). \tag{12}$$

In a later lecture of space-time symmetry, we can prove that U should be a unitary linear operator. Now, we assume it is true. We require the following properties for $U(\vec{R})$:

1. $U(0) = 1$.

2. $\langle\Psi^R| = \langle\Psi|U^\dagger(\vec{R})$

3. $\langle\Psi^R|\Psi^R\rangle = \langle\Psi|\Psi\rangle, \longrightarrow U^\dagger(\vec{R})U(\vec{R}) = 1$.

4. $\langle\Psi^R|\hat{\vec{r}}|\Psi^R\rangle = \langle\Psi|\hat{\vec{r}}+\vec{R}|\Psi\rangle \longrightarrow U^\dagger(\vec{\delta})\hat{\vec{r}}U(\vec{\delta}) = \hat{\vec{r}}+\vec{R}$.

5. $\langle\Psi^R|\hat{\vec{P}}|\Psi^R\rangle = \langle\Psi|\hat{\vec{P}}|\Psi\rangle \longrightarrow U^\dagger(\vec{R})\hat{\vec{P}}U(\vec{R}) = \hat{\vec{P}}$.
6. $\langle\Psi^R|\hat{\vec{S}}\Psi^R\rangle = \langle\Psi|\hat{\vec{S}}|\Psi\rangle \longrightarrow U^\dagger(\vec{R})\hat{\vec{S}}U(\vec{R}) = \hat{\vec{S}}$.
7. For two subsystems $|\psi_A\rangle$ and $|\psi_B\rangle$, we have $U_{AB}(\vec{R})[|\psi_A\rangle\otimes|\psi_B\rangle] = [U_A(\vec{R})|\psi_A\rangle]\otimes[U_B(\vec{R})|\psi_B\rangle]$.
8. We also fix the convention of the phase of U. For coordinate eigenstate $|\vec{r}^{\,\prime}\rangle$, whose wavefunction in the coordinate representation is $\delta(\vec{r}-\vec{r}^{\,\prime})$, $U|\vec{r}^{\,\prime}\rangle = |\vec{r}^{\,\prime}+\vec{R}\rangle$.

Consider an infinitesimal translation with $\vec{\delta}\sim 0$, and thus $U(\vec{\delta}) = 1+\vec{\delta}\cdot\frac{\partial U(\vec{\delta})}{\partial\vec{\delta}}$, we have

$$\langle\Psi(t)|U(\vec{\delta})|\Psi(t)\rangle \approx \langle\Psi(t)|\Psi(t)\rangle + \vec{\delta}\cdot\langle\Psi(t)|\frac{\partial U(\vec{\delta})}{\partial\vec{\delta}}|\Psi(t)\rangle. \tag{13}$$

If the space is translationally invariant, which means that if $|\Psi(t)\rangle$ represents a possible time-dependent state of the system, so does $|\Psi^{\prime}(t)\rangle = U(\delta)|\Psi(t)\rangle$. We also assume the time translation symmetry of the system, then $\langle\Psi(t)|\Psi^{\prime}(t)\rangle$ should be independent of t. Thus, $\langle\Psi|\frac{\partial U(\vec{\delta})}{\partial\vec{\delta}}|\Psi\rangle$ is a conserved quantity associated with space translation symmetry. Furthermore, for two subsystems with states $|\psi_A\rangle$ and $|\psi_B\rangle$, $\frac{\partial U(\vec{\delta})}{\partial\delta}$ is additive, *i.e.*,

$$\langle\psi_{AB}|\frac{\partial U_{AB}(\vec{\delta})}{\partial\vec{\delta}}|\Psi_{AB}\rangle = \langle\psi_A|\frac{\partial U_A(\vec{\delta})}{\partial\vec{\delta}}|\Psi_A\rangle + \langle\psi_B|\frac{\partial U_B(\vec{\delta})}{\partial\vec{\delta}}|\Psi_B\rangle. \tag{14}$$

From above properties, $\frac{\partial U(\vec{\delta})}{\partial\vec{\delta}}$ should be proportional to the total momentum up to a constant

$$\hat{\vec{P}} = iC\frac{\partial U(\vec{\delta})}{\partial\vec{\delta}}|_{\delta=0}. \tag{15}$$

P is a Hermitian operator. Later, we will prove that C is actually just $\hbar$. Let us use it now.

For simplicity, let us consider one-dimensional translation and drive its operator for finite distance translation R. From Eq. 15, we have

$$U(R+\delta) = U(R)U(\delta) \approx U(R)(1-\frac{i}{\hbar}p\delta) \tag{16}$$

and thus

$$\frac{\partial}{\partial_R}U(\vec{R}) = -\frac{ip}{\hbar}U(\vec{R}), \tag{17}$$

and thus

$$U(R) = e^{-\frac{i}{\hbar}pR}. \tag{18}$$

For the 3-dimensional translation, we can generalize the above result as

$$U(\vec{R}) = \exp\{-\frac{i}{\hbar}\vec{R}\cdot\vec{P}\}, \tag{19}$$

where $\vec{R}$ is a 3-vector.

Now let us consider the coordinate eigenstate $|\vec{r}\rangle$. The effect of an infinitesimal translation along the x-direction is

$$U(\delta\hat{e}_x)|\vec{r}\rangle = |\vec{r}+\delta\hat{e}_x\rangle \approx (1-\frac{i}{\hbar}\hat{P}_x\delta)|\vec{r}\rangle. \tag{20}$$

Then we have

$$\hat{P}_x|\vec{r}\rangle \quad = \quad \imath\hbar\vec{\nabla}_x|\vec{r}\rangle. \tag{21}$$

Please note that $\vec{\nabla}_{r_i}$ here is not an operator, it is just a derivative with respect to eigenvalues of $\vec{r}_1$, i.e.,

$$\nabla_x|\vec{r}\rangle = \lim_{\delta\to 0}\frac{|\vec{r}+\delta\hat{e}_x\rangle - |\vec{r}\rangle}{\delta}. \tag{22}$$

Then we have

$$\langle\vec{r}|\hat{P}_x|\Psi\rangle = \overline{\langle\Psi|\hat{P}_x|\vec{r}\rangle} = -i\hbar\nabla_x\langle\vec{r}|\Psi\rangle. \tag{23}$$

In terms of wavefunctions, we have

$$(\hat{P}_x\Psi)(\vec{r}) = -i\hbar\nabla_x\Psi(\vec{r}), \tag{24}$$

or, more generally,

$$(\hat{P}_i\Psi)(\vec{r}) = -i\hbar\nabla_i\Psi(\vec{r}). \tag{25}$$

We also have the expression for coordinates before

$$(x_i\Psi)(\vec{r}) = x_i\Psi(\vec{r}). \tag{26}$$

So far, we have both expressions of $\vec{x}$ and $\vec{P}$ in the coordinate representation.

4 Canonical quantization condition

For simplicity, let us consider a single particle, and we have

$$U^\dagger(\vec{\delta})\hat{r}U(\vec{\delta}) = \hat{r}+\vec{\delta}, \quad U^\dagger(\vec{\delta})\hat{p}U(\vec{\delta}) = \hat{p}, \quad U = \exp\{-\frac{i}{\hbar}\vec{\delta}\cdot\vec{P}\}. \tag{27}$$

From $U(\delta_x e_x)\hat{r}U(\delta_x e_x) = \hat{r} + \delta_x$, or,

$$U^\dagger(\delta_x e_x)\hat{x}U(\delta_x e_x) = \hat{x} + \delta_x, \tag{28}$$
$$U^\dagger(\delta_x e_x)\hat{y}U(\delta_x e_x) = \hat{y}, \tag{29}$$
$$U^\dagger(\delta_x e_x)\hat{z}U(\delta_x e_x) = \hat{z}. \tag{30}$$

Taking the limit of $\delta_x \to 0$, we have

$$[\hat{x}, \hat{p}_x] = i\hbar, \quad [\hat{x}, \hat{p}_y] = 0, \quad [\hat{x}, \hat{p}_z] = 0. \tag{31}$$

In general, we have

$$\hat{x}_i^\dagger = \hat{x}_i, \quad \hat{p}_i^\dagger = \hat{p}_i, \quad [\hat{x}_i, \hat{p}_j] = i\hbar\delta_{ij}. \tag{32}$$

This is the quantization condition in the Schödinger picture.

5 Momentum operators in many-particle systems

Now consider a many-particle system, their coordinate eigenstates $|\vec{r}_1, \vec{r}_2, ...\rangle$. The effect of the translation operator is

$$U(\vec{R})|\vec{r}_1, \vec{r}_2, ...\rangle = |\vec{r}_1 + \vec{R}, \vec{r}_2 + \vec{R}, ...\rangle. \tag{33}$$

and

$$U(\vec{R}) = e^{-\frac{i}{\hbar}\vec{R}\cdot\vec{P}_{tot}} \tag{34}$$

where $\vec{P}_{tot}$ is the total angular momentum defined as

$$\vec{P}_{tot} = \sum_i \vec{P}_i. \tag{35}$$

The we have

$$\vec{P}_{tot}|\vec{r}_1, \vec{r}_2, ...\rangle = \imath\hbar \sum_{r_i} \vec{\nabla}_{r_i} |\vec{r}_1, \vec{r}_2, ...\rangle. \tag{36}$$

Again we have

$$\langle \vec{r}_1, \vec{r}_2, ...|\hat{P}_{tot}|\Psi\rangle = \overline{\langle \Psi|\hat{P}_{tot}|\vec{r}_1, \vec{r}_2, ...\rangle} = -i\hbar \sum_i \nabla_i \langle \vec{r}_1, \vec{r}_2, ...|\Psi\rangle. \tag{37}$$

From the additivity of momentum, the momentum for the j-th particle should be

$$\langle \vec{r}_1, \vec{r}_2, ...|\vec{p}_j|\Psi\rangle = -i\hbar\vec{\nabla}_j \langle \vec{r}_1, \vec{r}_2, ...|\Psi\rangle, \tag{38}$$

, or, in terms of wavefunctions, we have

$$(\hat{p}_j \Psi)(\vec{r}_1, \vec{r}_2, ..) = -i\hbar \vec{\nabla}_j \Psi(\vec{r}_1, \vec{r}_2, ..). \tag{39}$$

6 Proof of $C = \hbar$

Recall that in Eq. 15, we set the value of $C = \hbar$. Now let us do actually prove it, and thus the canonical quantization condition does not bring a new constant other than $\hbar$. Consider a classic Hamiltonian $H(x, p)$, and we replace x and p with quantum mechanical operators $\hat{x}$ and $\hat{p}$ and then arrive at quantum mechanical Hamiltonian $\hat{H}(\hat{x}, \hat{p})$. Consider that in the case that $\hat{H}(\hat{x}, \hat{p})$ can be expanded as series of $\hat{x}$ and $\hat{p}$,

$$\hat{H}(\hat{x}, \hat{p}) = \sum_{n=1}^{+\infty} a_n \hat{p}^n + \sum_{m=1}^{+\infty} b_m \hat{x}^m. \tag{40}$$

We have

$$[\hat{x}, \hat{H}(\hat{x}, \hat{p})] = iC \frac{\partial \hat{H}(\hat{x}, \hat{p})}{\partial p}, \quad [\hat{p}, \hat{H}(\hat{x}, \hat{p})] = -iC \frac{\partial \hat{H}(\hat{x}, \hat{p})}{\partial x}. \tag{41}$$

Exercise Please prove Eq. 41.

Then from Schrödinger equation $i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle$, we have

$$\begin{aligned} \frac{d}{dt} \langle \Psi(t) | \hat{x}_j | \Psi(t) \rangle &= \frac{i}{i\hbar} \langle \Psi(t) | [\hat{x}_j, H] | \Psi(t) \rangle = \frac{C}{\hbar} \langle \Psi | \frac{\partial \hat{H}}{\partial p} | \Psi \rangle, \\ \frac{d}{dt} \langle \Psi(t) | \hat{p}_j | \Psi(t) \rangle &= \frac{i}{i\hbar} \langle \Psi(t) | [\hat{p}_j, H] | \Psi(t) \rangle = -\frac{C}{\hbar} \langle \Psi | \frac{\partial \hat{H}}{\partial x} | \Psi \rangle. \end{aligned} \tag{42}$$

Compared to the classic Hamilton equations, we conclude that $C = \hbar$. Thus Schrödinger equation plus quantization condition give rise to a harmonic correspondence between quantum and classic mechanics.

7 Momentum eigenstates and momentum representation

Consider a single particle momentum eigenstate $\hat{p}|\vec{p}\rangle = \vec{p}|\vec{p}\rangle$. In the coordinate representation, we have

$$\langle \vec{r} | \hat{p} | \vec{p} \rangle = \vec{p} \langle \vec{r} | \vec{p} \rangle, \tag{43}$$

or,

$$-i\hbar \nabla \psi_{\vec{p}}(\vec{r}) = \vec{p} \psi_{\vec{p}}(\vec{r}), \tag{44}$$

and thus we have

$$\psi_{\vec{p}}(\vec{r}) = \frac{1}{(2\pi)^{\frac{3}{2}}} e^{\frac{i}{\hbar}\vec{p}\cdot\vec{r}}. \tag{45}$$

Eq. 45 is normalized according to

$$\int d^3 r \psi^*_{\vec{p}}(\vec{r})\psi_{\vec{p}}(\vec{r}) = \delta(\vec{k} - \vec{k}^{\prime}), \tag{46}$$

where $\vec{k} = \vec{p}/\hbar$ is the wavevector. If we consider a finite volume, say, a cubic box with edge length L, the values of k_i are discrete, we use the box renormalization

$$\psi_{\vec{k}}(\vec{r}) = \frac{1}{L^{\frac{3}{2}}} e^{i\vec{k}\cdot\vec{r}}, \quad \int d^3 r \psi^*_{\vec{k}}(\vec{r})\psi_{\vec{k}}(\vec{r}) = \delta_{\vec{k},\vec{k}^{\prime}}. \tag{47}$$

Just like that all the eigenstates of $\hat{x}$ form a complete basis of a single particle Hilbert space, so do the eigenstates of $\hat{p}$. Similar results apply to many-particle systems. Let us denote $|p_1 p_2 ....\rangle$ as the eigenbases of a set of momenta operator $\hat{p}_1, \hat{p}_2, ...$ They satisfy

$$\begin{aligned}
\hat{p}_j|p_1 p_2 ...\rangle &= p_j|p_1 p_2 ...\rangle \\
\langle p_1 p_2 ...|p_1^{\prime} p_2^{\prime} ...\rangle &= \delta(p_1 - p_1^{\prime})\delta(p_2 - p_2^{\prime})... \\
\int dp_1 dp_2 ... |p_1 p_2 ..\rangle\langle p_1 p_2 ..| &= I.
\end{aligned} \tag{48}$$

For simplicity, let us come back to the single particle cases, and ask what are the expressions of wavefunctions, $\hat{x}$, and $\hat{p}$ in the momentum representation? The wavefunction of the state vector $|\Psi\rangle$ in momentum representation is

$$\Psi(\vec{p}) = \langle \vec{p}|\Psi\rangle. \tag{49}$$

And notice that $\hat{x}|x\rangle = x|x\rangle$, and $\langle p|\hat{p} = p\langle p|$, we have

$$\begin{aligned}
\langle p|\hat{x}|\Psi\rangle &= \int dx \langle p|\hat{x}|x\rangle\langle x|\Psi\rangle = \int dx x\langle p|x\rangle\langle x|\Psi\rangle = \int dx x e^{-i\frac{px}{\hbar}}\langle x|\Psi\rangle, \\
&= i\hbar\nabla_p \int dx \langle p|x\rangle\langle x|\Psi\rangle = i\hbar\nabla_p \Psi(p),
\end{aligned} \tag{50}$$

$$\langle p|\hat{p}|\Psi\rangle = p\Psi(p). \tag{51}$$

The above equations mean that in the momentum representation

$$\hat{x} = i\hbar\nabla_p, \quad \hat{p} = p. \tag{52}$$

8 Some subtle points

From Eq. 50, we have

$$\langle p|x|\Psi\rangle = i\hbar \lim_{\delta p \to 0} \frac{\langle p+\delta p|\Psi\rangle - \langle p|\Psi\rangle}{\delta p}, \tag{53}$$

thus

$$\langle p|x = i\hbar \nabla_p \langle p|, \tag{54}$$

or

$$x|p\rangle = -i\hbar \nabla_p |p\rangle. \tag{55}$$

Compare the expression proved before

$$p|x\rangle = i\hbar \nabla_x |x\rangle. \tag{56}$$