§3.3 Equation of Motion — Schrödinger Equation

11. QM principle of motion describes the time evolution of the state of a system, which is governed by the Schrödinger Equation:

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

where $|\psi(t)\rangle$ is the state vector, $\hat{H}(t)$ is the observable associated with the total energy of the system (called the Hamiltonian operator of the system), $\hbar$ is Planck constant divided by 2π, and $\frac{d}{dt}$ is to take derivative of time.

(1) The Schrödinger equation is a fundamental equation for the Quantum Mechanics, just like the Newtonian equation in the classical mechanics. In principle, it cannot be derived or proven from more fundamental principles, but it can only be verified by experiments. The Schrödinger equation describes the change of state with time, the time evolution of motion, or the change of motion.

(2) The Hamiltonian operator $\hat{H}$ comes from the classical Hamiltonian:

$$H(t) = \frac{\vec{P}_{(t)}^{\,2}}{2m} + V(t),$$

where $\vec{P}(t)$ is the momentum, m is the mass, and $V(t)$ is the potential energy of the system. $\frac{\vec{P}^2}{2m}$ represents the kinetic energy of the system. In QM, the Hamiltonian operator is given by

$$\hat{H}(t) = \frac{\hat{\vec{P}}_{(t)}^{\,2}}{2m} + \hat{V}(t).$$

(3) Note that the Schrödinger equation is expressed in the abstract state space with an abstract operator $\hat{H}$, abstract state vector $|\psi(t)\rangle$, and a full derivative $\frac{d}{dt}$

When express the Schrödinger Equation in any representation, it will become a partial derivative $\frac{\partial}{\partial t}$, and $\hat{H}(t)$ and $|\psi(t)\rangle$ will also be projected to this representation. The equation may not be such simple format, depending on what representation is chosen.

(4) The Schrödinger equation is of first order in t. From this it follows that, given the initial state $|\psi(t_0)\rangle$, the state $|\psi(t)\rangle$ at any subsequent time t is determined. There is no indeterminacy in the time evolution of a quantum system. Indeterminacy appears only when a physical quantity is measured, the state vector then undergoing an unpredictable modification (i.e., the reduction of the state to an eigenstate). However, between two measurements, the state vector evolves in a perfectly deterministic way, in accordance with the Schrödinger equation.

(5) The Schrödinger Equation is linear and homogeneous. It follows that its solution is linearly superposable.

Let $|\psi_1(t)\rangle$ and $|\psi_2(t)\rangle$ be two solutions of the Schrödinger equation:

$$i\hbar \frac{d}{dt}|\psi_1\rangle = \hat{H}\,|\psi_1\rangle$$

$$i\hbar \frac{d}{dt}|\psi_2\rangle = \hat{H}\,|\psi_2\rangle.$$

Then the linear superposition of $|\psi_1(t)\rangle$ and $|\psi_2(t)\rangle$:
$|\psi(t)\rangle = \lambda_1|\psi_1(t)\rangle + \lambda_2|\psi_2(t)\rangle$ (λ_1 and λ_2 are two complex constants) is also a solution to the Schrödinger Equation: $i\hbar\frac{d}{dt}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle$.

The statement can be verified as below:

$$i\hbar \frac{d}{dt}|\psi\rangle = \lambda_1 i\hbar \frac{d}{dt}|\psi_1\rangle + \lambda_2 i\hbar \frac{d}{dt}|\psi_2\rangle$$
$$= \lambda_1 \hat{H}|\psi_1\rangle + \lambda_2 \hat{H}|\psi_2\rangle$$
$$= \hat{H}(\lambda_1|\psi_1\rangle + \lambda_2|\psi_2\rangle)$$
$$= \hat{H}|\psi\rangle$$

Thus, the superposition $|\psi\rangle$ is a solution to the Schrödinger equation.

(6) The norm of the state vector $|\psi(t)\rangle$ is defined as $\sqrt{\langle\psi(t)|\psi(t)\rangle}$. Since the Hamiltonian operator $\hat{H}(t)$ is a Hermitian, i.e., $\hat{H}(t) = \hat{H}^*(t)$, the square of the norm of the state vector, $\langle\psi(t)|\psi(t)\rangle$, does not depend on t as we can see below:

$$\frac{d}{dt}\langle\psi(t)|\psi(t)\rangle = \left[\frac{d}{dt}\langle\psi(t)|\right]|\psi(t)\rangle + \langle\psi(t)|\left[\frac{d}{dt}|\psi(t)\rangle\right].$$

From the Schrödinger equation, we have $\frac{d}{dt}|\psi(t)\rangle = \frac{1}{i\hbar}\hat{H}|\psi(t)\rangle$, and $\frac{d}{dt}\langle\psi(t)| = -\frac{1}{i\hbar}\langle\psi(t)|\hat{H}^* = -\frac{1}{i\hbar}\langle\psi(t)|\hat{H}$.

Substituting these two items into above derivative equation, we have

$$\frac{d}{dt}\langle\psi(t)|\psi(t)\rangle = -\frac{1}{i\hbar}\langle\psi(t)|\hat{H}|\psi(t)\rangle + \frac{1}{i\hbar}\langle\psi(t)|\hat{H}|\psi(t)\rangle$$
$$= 0$$

Therefore, $\langle\psi(t)|\psi(t)\rangle = \langle\psi(t_0)|\psi(t_0)\rangle = 1.$

The last equality comes if the state vector $|\psi_0(t)\rangle$ is normalized at time t_0.

The property of the norm conservation is very useful in quantum mechanics. For example, it becomes indispensable when we interpret the square of the modulus $|\psi(\vec{r},t)|^2 = |\langle\vec{r}|\psi\rangle|^2$ of the wave function of a spinless particle as being the position probability density. Time evolution does not modify the global probability of finding the particle in all space, which alway remains equal to 1. Therefore,

$$\langle\psi(t)|\psi(t)\rangle = \int d^3r\,|\psi(\vec{r},t)|^2 = 1.$$

12. QM Commutation Relation.

Consider coordinate $\hat{x}$ and momentum $\hat{P}_x$; $\hat{P}_x = -i\hbar\frac{\partial}{\partial x}$ in the $\{|x\rangle\}$ representation. For any arbitrary state $|\psi\rangle$ in the $\{|x\rangle\}$ representation $\psi(x)$,

$$\begin{aligned}
\hat{P}_x \hat{x}\, \psi(x) &= \hat{P}_x [\hat{x}\, \psi(x)] \\
&= -i\hbar\frac{\partial}{\partial x} [x\, \psi(x)] \\
&= -i\hbar\left(\frac{\partial}{\partial x} x\right) \psi(x) - i\hbar\, x \frac{\partial}{\partial x}\psi(x) \\
&= -i\hbar\, \psi(x) - x \cdot i\hbar \frac{\partial}{\partial x}\psi(x) \\
&= (-i\hbar + \hat{x}\hat{P}_x)\, \psi(x).
\end{aligned}$$

$$\therefore (\hat{x}\hat{P}_x - \hat{P}_x\hat{x})\, \psi(x) = i\hbar\, \psi(x)$$

Since $\psi(x)$ is arbitrary, we conclude that

$$\hat{x}\hat{P}_x - \hat{P}_x\hat{x} = i\hbar$$

Define $[\hat{x}, \hat{P}_x] = \hat{x}\hat{P}_x - \hat{P}_x\hat{x}$,

$\therefore \quad [\hat{x}, \hat{P}_x] = i\hbar.$ $\qquad$ But $[\hat{x}, \hat{P}_y] = 0$

....

Similarly, $\quad [\hat{y}, \hat{P}_y] = i\hbar$

$\quad [\hat{z}, \hat{P}_z] = i\hbar$

$$\therefore [\hat{r}_i, \hat{P}_j] = i\hbar\,\delta_{ij} \quad (i, j = x, y, z)$$

Most operators are not commuting with each other. So you are NOT supposed to switch their orders when doing calculation. $[\hat{r}_i, \hat{P}_j] = i\hbar\,\delta_{ij}$, or $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ is called the commutation relation.

§3.4 Principle of Uncertainty — Indeterminacy

13. QM Principle of Uncertainty is a fundamental principle in Quantum Mechanics. It puts a fundamental limit on the accuracy of simultaneously determining the numerical values of two non-commuting observables. When these two non-commuting observables are a canonical coordinate and momentum of a particle, the product of the uncertainties of the coordinate and momentum is given by

$$\Delta Q \cdot \Delta P \geq \frac{\hbar}{2},$$ where Q is coordinate and P is momentum.

This relation is called the Heisenberg's Principle of Uncertainty or Heisenberg's uncertainty relation.

(1) The interpretation of this uncertainty relation is as follows: it is impossible to define at a given time both the position of the particle and its momentum to an arbitrary degree of accuracy. When the lower limit imposed by above relation is reached, increasing the accuracy in the position (decreasing ΔQ) implies that the accuracy in the momentum diminishes (increasing ΔP), and vice versa.

The limitation expressed by this uncertainty relation arises from the fact that the Planck constant h is not zero. It is the very small value of h $(= 6.626 \times 10^{-34}\,\text{J}\cdot\text{s})$ on the macroscopic scale that renders this limitation totally negligible in classical mechanics, but has considerable effect in microscopic world.

For example, let us consider a dust particle with a diameter on the order of $1\,\mu m$ and mass $m \approx 10^{-15}\,kg$, having a speed $v = 10^{-3}\,m/s$. Its momentum is then equal to

$$p = mv = 10^{-8}\ kg\cdot m/s.$$

If its position is measured to within $0.01\,\mu m$, then the uncertainty Δp in the momentum must satisfy

$$\Delta p \gtrsim \frac{\hbar/2}{\Delta Q} \approx \frac{10^{-34}}{10^{-8}} = 10^{-26}\ kg\cdot m/s, \text{ i.e., } \frac{\Delta p}{p} \gtrsim 10^{-8}.$$

Such a small uncertainty is totally negligible in the macroscopic world, as in practice, a momentum measurement device is incapable of attaining the required relative accuracy of 10^{-8}. In the macro world, we can regard $h \to 0$, so a particle can still have accurate position and momentum simultaneously, i.e., a certain motion orbit.

Now let us consider the microscopic world, for example, the hydrogen atom. Assume the electron is moving along the n_1 orbit, and position uncertainty $\Delta x \sim a_1 = 0.53 \times 10^{-10}\,m$. The momentum uncertainty is given by

$$\Delta p \geq \frac{\hbar/2}{\Delta x} = \frac{6.626\times 10^{-34}/2}{0.53\times 10^{-10}} = 6.25\times 10^{-24}\ kg\cdot m/s.$$

However, the momentum of the electron itself is given by

$$p = m_e v_1 = m_e\sqrt{\frac{e^2}{4\pi\varepsilon_0 m_e a_1}} = e\sqrt{\frac{m_e}{4\pi\varepsilon_0 a_1}}$$

$$= 1.6\times 10^{-19} \times \sqrt{\frac{9.1\times 10^{-31}}{4\pi\times 8.85\times 10^{-12}\times 0.53\times 10^{-10}}}$$

$$= 2.0\times 10^{-24}\ kg\cdot m/s.$$

Thus, $\dfrac{\Delta p}{p} \gtrsim \dfrac{6.25\times 10^{-24}}{2.0\times 10^{-24}} \simeq 3$, i.e., $\dfrac{\Delta p}{p} \geq 300\%$!

The relative uncertainty is so large that we cannot tell how much the electron momentum is !!!

(2) Derivation of Uncertainty Relation from commutation relation:

First, we need a precise definition of the uncertainties of the coordinate Q and momentum P. The uncertainties ΔQ and ΔP are defined as the root-mean-square deviation given by

$$\Delta Q = \sqrt{\langle (\hat{Q} - \langle \hat{Q} \rangle)^2 \rangle}$$

$$\Delta P = \sqrt{\langle (\hat{P} - \langle \hat{P} \rangle)^2 \rangle}$$

where, " $\langle\ \rangle$ " means taking mean, e.g., $\langle \hat{Q} \rangle = \langle \psi | \hat{Q} | \psi \rangle$, $|\psi\rangle$ is an arbitrary state vector

Now let us assume $|\psi\rangle$ is an arbitrary state but normalized, i.e., $\langle \psi | \psi \rangle = 1$. Operators corresponding to the coordinate and momentum are $\hat{Q}$ and $\hat{P}$. Consider the ket vector

$$|\varphi\rangle = (\hat{Q} + i\lambda \hat{P})|\psi\rangle,$$ where λ is an arbitrary real number.

The conjugate of $|\varphi\rangle$ is $\langle \varphi | = |\varphi\rangle^* = \langle \psi | (\hat{Q}^* - i\lambda^* \hat{P}^*)$

Since $\hat{Q}$ and $\hat{P}$ are Hermitian, i.e., $\hat{Q} = \hat{Q}^*$, $\hat{P} = \hat{P}^*$, we have

$$\langle \varphi | = \langle \psi | (\hat{Q} - i\lambda \hat{P}).$$

For all λ, the square of the norm $\langle \varphi | \varphi \rangle$ is positive, i.e.,

$$\begin{aligned}
\langle \varphi | \varphi \rangle &= \langle \psi | (\hat{Q} - i\lambda \hat{P})(\hat{Q} + i\lambda \hat{P}) | \psi \rangle \\
&= \langle \psi | \hat{Q}^2 + i\lambda \hat{Q}\hat{P} - i\lambda \hat{P}\hat{Q} + \lambda^2 \hat{P}^2 | \psi \rangle \\
&= \langle \psi | \hat{Q}^2 | \psi \rangle + i\lambda \langle \psi | \hat{Q}\hat{P} - \hat{P}\hat{Q} | \psi \rangle + \lambda^2 \langle \psi | \hat{P}^2 | \psi \rangle \\
&= \langle \hat{Q}^2 \rangle + i\lambda \langle [\hat{Q}, \hat{P}] \rangle + \lambda^2 \langle \hat{P}^2 \rangle \\
&= \langle \hat{Q}^2 \rangle - \hbar\lambda + \langle \hat{P}^2 \rangle \lambda^2 \geq 0.
\end{aligned}$$

Recall the commutation relation $[\hat{Q}, \hat{P}] = i\hbar$.

For polynomial expression $\langle \hat{Q}^2 \rangle - \hbar\lambda + \langle \hat{P}^2 \rangle \lambda^2 \geq 0$, the discriminant of this expression must be negative or zero:

[Discriminant for quadratic $ax^2 + bx + c = 0$ is $(b^2 - 4ac)$.]

$\hbar^2 - 4\langle\hat{P}^2\rangle\langle\hat{Q}^2\rangle \leq 0.$

Therefore, we have $\langle\hat{Q}^2\rangle\langle\hat{P}^2\rangle \geq \frac{\hbar^2}{4}.$

Now define $\hat{Q}' = \hat{Q} - \langle\hat{Q}\rangle$, $\hat{P}' = \hat{P} - \langle\hat{P}\rangle$.

Then we find $\hat{Q}'$ and $\hat{P}'$ have the same commutation relation as $\hat{Q}$ and $\hat{P}$: $[\hat{Q}', \hat{P}'] = i\hbar$

$$
\begin{aligned}
[\hat{Q}', \hat{P}'] &= \hat{Q}'\hat{P}' - \hat{P}'\hat{Q}' \\
&= (\hat{Q} - \langle\hat{Q}\rangle)(\hat{P} - \langle\hat{P}\rangle) - (\hat{P} - \langle\hat{P}\rangle)(\hat{Q} - \langle\hat{Q}\rangle) \\
&= (\hat{Q}\hat{P} - \hat{Q}\langle\hat{P}\rangle - \langle\hat{Q}\rangle\hat{P} + \langle\hat{Q}\rangle\langle\hat{P}\rangle) \\
&\quad - (\hat{P}\hat{Q} - \hat{P}\langle\hat{Q}\rangle - \langle\hat{P}\rangle\hat{Q} + \langle\hat{P}\rangle\langle\hat{Q}\rangle) \\
&= \hat{Q}\hat{P} - \hat{P}\hat{Q} = [\hat{Q}, \hat{P}] = i\hbar.
\end{aligned}
$$

Recall $\langle\hat{Q}\rangle$ and $\langle\hat{P}\rangle$ are mean numbers, so they can switch order with each other or switch order with $\hat{Q}$ and $\hat{P}$.

Therefore, going through the same procedure as $\hat{Q} + i\lambda\hat{P}$, the square of the norm $|\varphi'\rangle = (\hat{Q}' + i\lambda\hat{P}')|\psi\rangle$,

$$
\begin{aligned}
\langle\varphi'|\varphi'\rangle &= \langle(\hat{Q}')^2\rangle + i\lambda\langle[\hat{Q}', \hat{P}']\rangle + \lambda^2\langle(\hat{P}')^2\rangle \\
&= \langle(\hat{Q}')^2\rangle - \hbar\lambda + \langle(\hat{P}')^2\rangle\lambda^2 \geq 0
\end{aligned}
$$

$\therefore\ \hbar^2 - 4\langle(\hat{Q}')^2\rangle\langle(\hat{P}')^2\rangle \leq 0$

Therefore, $\langle(\hat{Q}')^2\rangle\langle(\hat{P}')^2\rangle \geq \frac{\hbar^2}{4}.$

According to the definition of uncertainty:

$$\Delta Q = \sqrt{\langle(\hat{Q} - \langle\hat{Q}\rangle)^2\rangle} = \sqrt{\langle(\hat{Q}')^2\rangle}$$

$$\Delta P = \sqrt{\langle(\hat{P} - \langle\hat{P}\rangle)^2\rangle} = \sqrt{\langle(\hat{P}')^2\rangle}$$

Therefore, $\Delta Q \cdot \Delta P = \sqrt{\langle(\hat{Q}')^2\rangle\langle(\hat{P}')^2\rangle} \geq \sqrt{\frac{\hbar^2}{4}} = \frac{\hbar}{2}.$

(3) The Heisenberg Uncentainty Principle can be generalized to the following: if two observables are conjugates (like the coordinate and momentum are conjugates with each other), there exists an exact lower bound for the product of uncertainties, which is equal to $\hbar/2$.

Further generalization of uncertainty relation is that two arbitrary observables $\hat{A}$ and $\hat{B}$ have such limitation:

$$\Delta A \cdot \Delta B \geqslant \frac{1}{2} \left| \langle [\hat{A}, B] \rangle \right| .$$

In other words, the mimimum bound of the product of uncertainties is determined by the commutation relation between these two observables. If $\hat{A}$ and $\hat{B}$ are commuting, i.e., $[\hat{A}, \hat{B}] = 0$, then $\Delta A \cdot \Delta B \geqslant 0$. This means that it is possible to Simultaneously determine $\hat{A}$ and $\hat{B}$ precisely.

But if $[\hat{A}, \hat{B}] \neq 0$, then there is a minimum limit on the accuracy of simultaneously determining $\hat{A}$ and $\hat{B}$.