Schrödinger Equation

In this lecture, we will discuss how the quantum state of a particle evolves with time — Schrödinger Equation.

The Schrödinger Equation cannot be derived. We will try to establish it based on the requirements for wave function of free particle. The correctness of the Schrödinger Equation can only be verified by comparing its prediction for various systems with experimental observation.
Schrödinger Equation

In classical physics, if we know the state of a particle at time $t_0$, we can then predict its motion at any time $t (> t_0)$. Similarly in quantum mechanics, if we know the state of the particle at a given time, its subsequent quantum states should be described by an appropriate equation.

In classical physics, the state of a particle is described by its position and velocity, and the equation of motion is the Newton’s equation. In quantum mechanics, however, the quantum state of a particle is described by a wave function. We therefore need an appropriate equation to describe how the wave function changes with time.
Requirements on the Equation

- It should be an equation involving the time derivative of the wave function, since it is to describe the time dependence of the wave function.

- The equation must be a linear equation. This is because if $\Psi_1$ and $\Psi_2$ are solutions of the equation, then the linear combination $c_1\Psi_1 + c_2\Psi_2$ is also a solution of the equation.

- The coefficients cannot contain quantities which depend on the state, such as energy, momentum, etc, otherwise, the applicability of the equation would be limited.

We now try to find an equation satisfying these conditions. We will consider free particle first and then extend it to general case.
Free Particle

Wave function of a free particle

\[ \Psi(r, t) = Ae^{i(p \cdot r - Et)/\hbar} \]

It’s time derivative is

\[ \frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar} E \Psi \]

(1)

This is still not the desired equation because its coefficients contain \( E \). Next differentiate with respect to coordinate variables and hope for elimination of \( E \).

\[ \frac{\partial \Psi}{\partial x} = \frac{ip_x}{\hbar} \Psi \]

\[ \frac{\partial^2 \Psi}{\partial x^2} = -\frac{p_x^2}{\hbar^2} \Psi \]

Similarly

\[ \frac{\partial^2 \Psi}{\partial y^2} = -\frac{p_y^2}{\hbar^2} \Psi, \quad \frac{\partial^2 \Psi}{\partial z^2} = -\frac{p_z^2}{\hbar^2} \Psi \]
Free Particle

Combine the three equations, we have

\[
\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} = \nabla^2 \Psi = -\frac{p^2}{\hbar^2} \Psi
\]  

(2)

For a free particle

\[
E = \frac{p^2}{2m}
\]  

(3)

Compare Eq.(1) and Eq.(2), we get

\[
i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi
\]

This equation satisfies all the requirements.
Schrödinger Equation

We can rewrite Eq.s. (1) and (2) as

\[ E\Psi = i\hbar \frac{\partial}{\partial t} \Psi \]

\[ (\vec{p} \cdot \vec{p}) \Psi = (-i\hbar \nabla) \cdot (-i\hbar \nabla) \Psi \]

where

\[ \nabla = \hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z} \]

The energy \( E \) and momentum \( \vec{p} \) of the particle are obtained by the operations of the following operators on the wave function, respectively.

\[
E \rightarrow i\hbar \frac{\partial}{\partial t}, \quad \vec{p} \rightarrow -i\hbar \nabla
\]

These operators are the energy and momentum operators, respectively.
Schrödinger Equation

Therefore, to construct the Schrödinger equation, we multiply both sides of Eq.(3) by $\Psi$ and then replace $E$ and $\vec{p}$ by the corresponding operators.

$$E \Psi = \frac{p^2}{2m} \Psi$$

\[ \Downarrow \]

$$E \rightarrow i\hbar \frac{\partial}{\partial t}, \quad \vec{p} \rightarrow -i\hbar \nabla$$

\[ \Downarrow \]

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi$$
Schrödinger Equation

If the particle is subject to a field and the potential energy of the particle is given by $U(\vec{r})$, then

$$E = \frac{p^2}{2m} + U(\vec{r})$$

The Schrödinger equation can be established by multiplying the above equation by $\Psi$ and then replacing $E$ and $\vec{p}$ by the corresponding operators, i.e.

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + U(\vec{r})\Psi$$

Introducing the Hamiltonian operator

$$H = -\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r})$$

The Schrödinger equation can be written as

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$$
System of Many Particles

Consider a system of \( N (> 1) \) particles. The coordinates of the particles are specified by \( \vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N \), and the corresponding momenta are \( \vec{p}_1, \vec{p}_2, \cdots, \vec{p}_N \). The wave function should be a function of the \( N \) variables \( \Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N, t) \).

The total energy of the system is

\[
E = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m_i} + U(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)
\]

Multiplying both sides of this equation by the wave function and making the following substitution

\[
E \rightarrow i \hbar \frac{\partial}{\partial t}, \quad \vec{p}_i \rightarrow -i \hbar \nabla_i
\]

where

\[
\nabla_i = \hat{i} \frac{\partial}{\partial x_i} + \hat{j} \frac{\partial}{\partial y_i} + \hat{k} \frac{\partial}{\partial z_i}
\]
System of Many Particles

We get the Schrödinger equation for a system of many particles

\[ i\hbar \frac{\partial \Psi}{\partial t} = H \Psi \]

\[ H = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \nabla_i^2 + U(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \]
Development of QM

1901  Planck  Blackbody radiation
1905  Einstein  Photoelectric effect
1913  Bohr  Quantum theory of spectra
1922  Compton  Scattering of photons off electrons
1924  Pauli  Exclusion principle
1925  de Broglie  Matter wave
1926  Schrödinger  Wave equation
1927  Heisenberg  Uncertainty principle
1927  Davisson  Experiment on wave properties of electron
& Germer
1927  Born  Interpretation of the wave function

Solving the Schrödinger equation:

1960s  Kohn  Density functional theory
       Hohenberg
       Sham
1980s  Car  Computational techniques
       Parrinello
       et al.