Schrödinger's equation

Postulates of quantum mechanics

de Broglie postulated that entities like electron are particles in the classical sense in that they carry energy and momentum in localized form; and at the same time they are wave-like, *i.e.* not completely point object, in that they undergo interference. de Broglie's *wave-particle duality* leads to associating electron and likes with the *wave function* $\psi(x,\, t)$ such that $|\psi(x,\, t)|^2$ gives the probability of finding them at $(x,\, t)$. A minimum uncertainty wave packet is an example of wave function asssociated with a particle localized over the region $x \pm \Delta x$ and having momenta spread over $k \pm \Delta k$. This wave function describes particle having a constant momentum range $k \pm \Delta k$ *i.e.* free particle – particle in absence of any force or potential. But if the particle is acted on by a force, its momentum is going to change and, therefore, free particle wave function is going to change too. The wave function of a particle $\psi(x,\, t)$ subjected to some force, specified by potential $V(x,\, t)$, is obtained by solving Schrödinger equation,

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} \;=\; -\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x,t)}{\partial x^2} + V(x,t)\,\psi(x,t). \tag{1}$$

Above is the 1-dimensional Schrödinger equation (for 3-dimension replace $\partial^2/\partial x^2$ by ∇^2 and x by $\vec{x}$). The Schrödinger equation (1) is a postulate of quantum mechanics. We can arrive at Schrödinger equation from a few *reasonable* assumptions,

1. the quantum mechanical wave equation must be consistent with de Broglie hypothesis $p = \hbar k$ and $E = \hbar\omega$,
2. that wave equation should obey the energy relation $E = p^2/2m + V$ (*i.e.* total energy = kinetic + potential energy),
3. and it must be linear in $\psi(x,t)$ so as to ensure linear superposition, implying if ψ_1 and ψ_2 are solutions of Schrödinger equation then $a\psi_1 + b\psi_2$ is also a solution for arbitrary a and b.

Consider plane wave description of a particle,

$$\psi(x,t) \;=\; A\,e^{i(kx-\omega t)} \quad \text{in 3} - \text{dimension} \quad \rightarrow \quad \psi(\mathbf{r},t) \;=\; A\,e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$$

which according to de Broglie hypothesis,

$$\psi(\mathbf{r},t) \;=\; A\,e^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar} \;=\; A\,e^{i(p_x x + p_y y + p_z z - Et)/\hbar}.$$

It is immediately obvious that $\psi(\mathbf{r},t)$ is eigen-function of the operators $i\hbar\,\partial/\partial t$, $-i\hbar\,\partial/\partial r_j$ and $-i\hbar\,\partial/\partial p_j$ with eigen-value E, p_j and r_j respectively,

$$\begin{aligned} i\hbar\frac{\partial\psi}{\partial t} &= E\,\psi \\ -i\hbar\frac{\partial\psi}{\partial x} &= p_x\psi \quad \text{etc.} \quad \rightarrow \; \mathbf{p} \;=\; -i\hbar\,\nabla \\ -i\hbar\frac{\partial\psi}{\partial p_x} &= x\psi \quad \text{etc.} \quad \rightarrow \; \mathbf{r} \;=\; -i\hbar\,\nabla_p \end{aligned}$$

At this point we postulate association between the dynamical quantities and the differential operators (in coordinate space)

$$\mathbf{r} \leftrightarrow \hat{\mathbf{r}}, \quad \mathbf{p} \leftrightarrow -i\hbar\nabla \equiv \hat{\mathbf{p}} \quad \text{and} \quad E \leftrightarrow i\hbar\frac{\partial}{\partial t} \equiv \hat{E} \tag{2}$$

which essentially amounts to postulating Schrödinger equation. Using this operator association in the energy relation, we obtain the operator equation,

$$-\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(\hat{\mathbf{r}}, t) = i\hbar\frac{\partial}{\partial t} \tag{3}$$

LHS of the above equation (3) is also known as *Hamiltonian* operator,

$$\hat{H} \equiv -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(\hat{\mathbf{r}}, t) \tag{4}$$

since for a closed system, Hamiltonian H represents the energy of the system which is the sum of kinetic and potential energy $H(q,p) = p^2/2m + V(q)$. If the Hamiltonian operator is made to act on particle wave function, we get Schrödinger equation, *i.e.* Hamiltonian generates time evolution of wave function,

$$\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t} \quad \Rightarrow \quad -\frac{\hbar^2}{2m}\nabla^2\psi + \hat{V}\psi = i\hbar\frac{\partial\psi}{\partial t}. \tag{5}$$

To get to know about the behavior of quantum particle in force field or potential, we have to solve the Schrödinger equation (5) for specific potentials and for the most part of this course we will confine ourselves to somewhat simplified setting (but of great interest nontheless) – solving 1-dimensional Schrödinger equation (1) for potentials not depending explicitly on time $V(x,t) \rightarrow V(x)$. In that case Schrödinger equation can be solved by *separation of variables*, where we seek solution of the form

$$\psi(x,t) = \psi(x)\,\varphi(t) \tag{6}$$

and then the partial differential equation (1) involving x and t reduces to two ordinary differential equations,

$$E\varphi(t) = i\hbar\frac{d\varphi(t)}{dt} \tag{7}$$

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\,\psi(x) \quad \Rightarrow \quad \hat{H}\psi(x) = E\,\psi(x). \tag{8}$$

The E is the *separation constant*, which can be shown to be exactly equal to total energy of the particle. The equation (8) is called 1-dimensional time-independent Schrödinger equation. The solution of equation (7) is easy $\varphi(t) = \exp(-iEt/\hbar)$ and the solution of Schrödinger equation (1) is

$$\psi(x,t) = \psi(x)\,e^{-iEt/\hbar}. \tag{9}$$

To know the full solution $\psi(x,t)$ we need to solve the time-independent Schrödinger equation (8) for specific potentials. Three important consequences of solutions obtained by separation of variables (6) are,

1. The solutions $\psi(x,t) = \psi(x)\,\exp(-iEt/\hbar)$ are *stationary states* implying probability density $|\psi(x,t)|^2$ and every expectation value are constant in time.
2. The states are of definite total energy.

$$\begin{aligned}\langle H\rangle &= \int \psi^\star \hat{H}\psi\,dx = E\int|\psi|^2 dx = E\\ \langle H^2\rangle &= \int \psi^\star \hat{H}^2\psi\,dx = E^2\int|\psi|^2 dx = E^2\\ &\Rightarrow\ \sigma_H^2 = \langle H^2\rangle - \langle H\rangle^2 = 0\end{aligned}$$

3. The general solution is a *linear combination* of separable solutions (each of which are stationary states),

$$\psi(x,t)\ = \sum_{n=1}^{\infty} c_n\psi_n(x,t)\ = \sum_{n=1}^{\infty} c_n\psi_n(x)\,e^{-iE_nt/\hbar}$$

Before embarking upon solving Schrödinger equation for varieties of potentials, we will explore a little more about the consequences of the postulates of quantum mechanics. Summarizing, the postulates of quantum mechanics thus are:

1. The wave function $\psi(x,t)$ describes motion of a particle in x and t in presence of potential, consistent with de Broglie's wave particle duality and uncertainty principle.
2. Each dynamical variables are associated with operators.
3. $\psi(x,t)$ are continuous, well-behaved, single-valued and square-integrable.
4. If a measurement is made at a certain time t to locate a particle, whose wave function is $\psi(x,t)$, then the probability $P(x,t)\,dx$ that the particle will be found in the interval x and $x+dx$ is,

$$P(x,t)\,dx\ =\ \psi^\star(x,t)\,\psi(x,t)\,dx\ =\ |\psi(x,t)|^2\,dx \quad\Rightarrow\quad \int_{-\infty}^{\infty} P(x,t)\,dx\ =\ 1.$$

5. The observables, *i.e.* those quantities that can be measured in experiments, are the expected average results of a system of statistical measurements

$$\langle\hat{\alpha}\rangle\ =\ \frac{\int\psi^\star\,\hat{\alpha}\,\psi\,dx}{\int\psi^\star\,\psi\,dx}.$$

6. Schrödinger equation is a linear, partial differential equation and if ψ_1 and ψ_2 are solutions of Schrödinger equation then $a_1\psi_1 + a_2\psi_2$ is also a solution for arbitrary a_1 and a_2. A possible physical state of a system is a linear superposition of many wave functions, each describing various permissible physical state of the system,

$$\psi\ =\ \sum_i a_i\,\psi_i.$$

The probability for this superposition, if the solutions ψ_i are orthonormal, is:

$$P = |\psi|^2 = \left| \sum_i a_i \psi_i \right|^2 = \sum_i |a_i|^2$$