Quantum Mechanics

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Lesson IV
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Time dependent Schrödinger equation

- It is not possible to derive the Schrödinger equation in any rigorous fashion from classical physics
- However ☞ it had to come from somewhere and it is indeed possible to "derive" the Schrödinger equation using somewhat less rigorous means
- Consider particle with mass m and momentum p_x moving in 1-dimension in potential $V(x)$ ☞ total energy is

$$E = \frac{p_x^2}{2m} + V(x) \tag{1}$$

- Multiplying both sides of (1) by wave function $\psi(x,t)$ should not change equality

$$E\psi(x,t) = \left[\frac{p_x^2}{2m} + V(x)\right]\psi(x,t) \tag{2}$$

Time dependent Schrödinger equation (cont'd)

- Recall de Broglie relations

$$p_x = \hbar k_x \quad \text{and} \quad E = \hbar\omega \tag{3}$$

- Suppose wave function is plane wave traveling in x direction with a well defined energy and momentum

$$\psi(x,t) = A_0 e^{i(k_x x - \omega t)} \tag{4}$$

- Energy relation in terms of de Broglie variables becomes

$$\hbar\omega A_0 e^{i(k_x x - \omega t)} = E A_0 e^{i(k_x x - \omega t)} \tag{5}$$

$$\left[\frac{\hbar^2 k_x^2}{2m} + V(x)\right] A_0 e^{i(k_x x - \omega t)} = \left[\frac{p_x^2}{2m} + V(x)\right] A_0 e^{i(k_x x - \omega t)} \tag{6}$$

Time dependent Schrödinger equation (cont'd)

- For equality in (5) to hold

$$E\psi(x,t) = i\hbar \frac{\partial}{\partial t}\psi(x,t) \tag{7}$$

- For equality in (6) to hold

$$p_x\psi(x,t) = -\hbar \frac{\partial}{\partial x}\psi(x,t) \tag{8}$$

Puttin'all this together ☞ time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t}\psi(x,t) = \left[-\frac{h^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x,t) \tag{9}$$

Time dependent Schrödinger equation (cont'd)

2nd-order linear differential equation with 3 important properties

- it is consistent with energy conservation
- it is linear and singular value ☞ solutions can be constructed by superposition of two or more independent solutions
- free-particle solution ☞ $V(x) = 0$
  consistent with a single de Broglie wave

Time independent Schrödinger equation

- If potential energy is independent of time
  use mathematical technique known as separation of variables
- Assume

$$\psi(x,t) = \psi(x)\,\chi(t) \tag{10}$$

- Substitution into time dependent Schrödinger equation yields

$$i\hbar\frac{\partial}{\partial t}\chi(t) = E\chi(t) = \hbar\omega\chi(t) \tag{11}$$

$$\left[-\frac{h^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right]\psi(x) = E\psi(x) \tag{12}$$

- Solution to (11) ☞ oscillating complex exponential

$$\chi(t) = e^{-iEt/\hbar} = e^{-i\omega t} \tag{13}$$

- Solution to (12) ☞ an eigenvalue problem

Time independent Schrödinger equation

2nd-order linear differential equation with 3 important properties

- *Continuity:* Solutions $\psi(x)$ to (12) and its first derivative $\psi'(x)$ must be continuous $\forall x$ (the latter holds for finite potential $V(x)$)
- *Normalizable:* Solutions $\psi(x)$ to (12) must be square integrable integral of modulus squared of wave function over all space must be finite constant so that wave function can be normalized

$$\int |\psi(x)|^2 \, dx = 1$$

- *Linearity:* Given two independent solutions $\psi_1(x)$ and $\psi_2(x)$ can construct other solutions by taking superposition of these

$$\psi(x) = \alpha_1 \, \psi_1(x) + \alpha_2 \, \psi_2(x)$$

$\alpha_i \in \mathbb{C}$ satisfying $|\alpha_1|^2 + |\alpha_2|^2 = 1$ to ensure normalization.

Born's rule

- Probability amplitude ψ ☞ complex function
  used to describe behaviour of systems
- Probability density (probability per unit length in one dimension)

$$P(x)\,dx = |\psi(x)|^2 dx \tag{14}$$

- Probability to find particle between two points x_1 and x_2

$$P(x_1 < x < x_2) = \int_{x_1}^{x_2} |\psi(x)|^2 \, dx \tag{15}$$

- Normalization ☞ probability to find particle between $(-\infty, +\infty)$

$$\int_{-\infty}^{+\infty} |\psi(x)|^2 \, dx = 1 \tag{16}$$

Expectation value

- We can no longer speak with certainty about particle position
- We can no longer guarantee outcome of single measurement
  (of any physical quantity that depends on position)
- Expectation value ☞
  most probable outcome for single measurement
  which is equivalent to average outcome for many measurements
- E.g. ☞ determine expected location of particle
  Performing a large number of measurements
  we calculate average position

$$\langle x \rangle = \frac{n_1 x_1 + n_2 x_2 + \cdots}{n_1 + n_2 + \cdots} = \frac{\sum_i n_i x_i}{\sum_i n_i} \tag{17}$$

Expectation value (cont'd)

- Number of times n_i that we measure each position x_i
  is proportional to probability $P(x_i)\,dx$
  to find particle in interval dx at x_i

- Making substitution and changing sums to integrals

$$\langle x \rangle = \frac{\int_{-\infty}^{+\infty} P(x)\, x\, dx}{\int_{-\infty}^{+\infty} P(x)\, dx} \Rightarrow \langle x \rangle = \int_{-\infty}^{+\infty} x |\psi(x)|^2\, dx \qquad (18)$$

- Expectation value of any function $f(x)$

$$\langle f(x) \rangle = \int_{-\infty}^{+\infty} f(x) |\psi(x)|^2\, dx \qquad (19)$$

Dirac notation

- State vector or wave-function ψ ☞ represented as "ket" $|\psi\rangle$
- We express any n-dimensional vector in terms of basis vectors
- We expand any wave function in terms of basis state vectors

$$|\psi\rangle = \lambda_1|\psi_1\rangle + \lambda_2|\psi_2\rangle + \cdots \tag{20}$$

- Alongside the ket ☞ we define "bra" $\langle\psi|$
- Together ☞ bra and ket define *scalar product*

$$\langle\phi|\psi\rangle \equiv \int_{-\infty}^{+\infty} dx\, \phi^*(x)\, \psi(x) \Rightarrow \langle\phi|\psi\rangle^* = \langle\psi|\phi\rangle \tag{21}$$

- As for n-dimensional vector ☞ Schwartz inequality holds

$$\langle\psi|\phi\rangle \leq \sqrt{\langle\psi|\psi\rangle\langle\phi|\phi\rangle} \tag{22}$$

Operators and Observables

- Operator $\hat{A}$ ☞ maps state vector into another $\hat{A}|\psi\rangle = |\phi\rangle$
- Eigenstate (or eigenfunction) of $\hat{A}$ with eigenvalue a

$$\hat{A}|\psi\rangle = a|\psi\rangle$$

- Observable ☞ any particle property that can be measured
- For any observable A ☞ there is an operator $\hat{A}$

$$\langle A \rangle = \langle \psi | \hat{A} | \psi \rangle = \int_{-\infty}^{+\infty} dx\, \psi^*(x)\, \hat{A}\psi(x) \tag{23}$$

- $A^\dagger$ is called hermitian conjugate of $\hat{A}$ if

$$\int_{-\infty}^{+\infty} (\hat{A}^\dagger \phi)^*\, \psi\, dx = \int_{-\infty}^{+\infty} \phi^*\, \hat{A}\psi\, dx \Rightarrow \langle A^\dagger \phi | \psi \rangle = \langle \phi | A \psi \rangle \tag{24}$$

- $\hat{A}$ is called hermitian if $\hat{A}^\dagger = \hat{A}$ ☞ $\langle A\phi | \psi \rangle = \langle \phi | A\psi \rangle$

Commutator

- Operators are associative but not (in general) commutative

$$\hat{A}\hat{B}|\psi\rangle = \hat{A}(\hat{B}\psi\rangle) = (\hat{A}\hat{B})|\psi\rangle \neq \hat{B}\hat{A}|\psi\rangle \tag{25}$$

- Example ☞ $$(\hat{x}\hat{p} - \hat{p}\hat{x})\psi(x) = -i\hbar\left\{x\frac{\partial\psi}{\partial x} - \frac{\partial}{\partial x}[x\psi(x)]\right\} \tag{26}$$

  by product rule of differentiation

$$(\hat{x}\hat{p} - \hat{p}\hat{x})\psi(x) = i\hbar\psi(x) \tag{27}$$

- Since this must hold for any function $\psi(x)$

$$\hat{x}\hat{p} - \hat{p}\hat{x} = i\hbar \tag{28}$$

- Short-hand notation:

$$[\hat{A},\hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}$$

- A "free" particle ☞ no external forces acting upon it $\Rightarrow V(x) = V_0$
- State represented by its wave function ☞ $\psi(x) = Ae^{ikx}$
- Schrödinger equation has 4 possible solutions

$$\frac{2m}{\hbar^2}(E - V_0)\psi(x) = -\frac{\partial^2}{\partial x^2}\psi(x) = k^2\psi(x) \qquad \pm k \in \Re \text{ or } \Im \tag{29}$$

  - 2 travelling waves solutions

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \qquad k = \pm\frac{1}{\hbar}\sqrt{2m(E - V_0)} \quad (E > V_0) \tag{30}$$

  - 2 exponentially decaying solutions

$$\psi(x) = Ae^{\kappa x} + Be^{-\kappa x} \qquad i\kappa = \pm i\frac{1}{\hbar}\sqrt{2m(V_0 - E)} \qquad (E < V_0) \tag{31}$$

- Allowed energies are

$$E = \frac{\hbar^2 k^2}{2m} + V_0 \tag{32}$$

- $E > V_0$ ☞ classically allowed
- $E < V_0$ ☞ classically forbidden
- Traveling wave solutions ☞ time evolution of probability density

$$P(x,t) = \psi^*(x,t)\psi(x,t) = \psi^*(x)e^{i\omega t}\psi(x)e^{-i\omega t} = \psi^*(x)\psi(x) \quad (33)$$

independent of time!

- Particle traveling in only one (say $+x$) direction

$$P(x,t) = \psi^*(x)\psi(x) = A^*e^{-ikx}Ae^{ikx} = A^*A \quad (34)$$

independent of position ☞ particle completely delocalized!

- Superposition of both positive and negative going waves

$$\begin{aligned} P(x,t) &= \left(Ae^{ikx} + B^{-ikx}\right)^* (Ae^{ikx} + Be^{-ikx}) \\ &= A^*A + B^*B + 2\Re\{A^*Be^{-2ikx} + B^*Ae^{2ikx}\} \end{aligned}$$

- For real-valued coefficients A and B

$$P(x,t) = A^2 + B^2 + 2ABcos(2kx) \quad (35)$$

which is equation for standing wave