Schrödinger equation

Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
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Max Born (1928) was the first to discover (by chance and with no theoretical foundation) that the square of the quantum wave equations (described by the wave structure of matter as mass-energy density of space) could be used to predict the probability of where the particle would be found. Since it was impossible for both the waves and the particles to be real entities, it became customary to regard the waves as unreal probability waves and to maintain the belief in the 'real' particle. Unfortunately (profoundly) this maintained the belief in the particle/wave duality, in a new form where the 'quantum' scalar standing waves had become 'probability waves' for the 'real' particle.

1. Derivation of Schrödinger equation

From the de Broglie hypothesis, a plane wave can be expressed by

$$\psi(r,t) = C\exp[i(\mathbf{k}\cdot\mathbf{r} - \omega t)].$$

This should be a solution of the free particle with mass *m;*

$$E = h\nu = \hbar\omega = \frac{p^2}{2m}$$

$$p = \hbar k = \frac{h}{\lambda}$$

Then we have

$$\psi(r,t) = C\exp[\frac{i}{\hbar}(\mathbf{p}\cdot\mathbf{r} - Et)]$$

We note that

$$i\hbar\frac{\partial}{\partial t}\psi(r,t) = E\psi(r,t) \qquad \text{or} \qquad E \to i\hbar\frac{\partial}{\partial t}$$

and

$$\frac{\partial}{\partial \mathbf{r}}\psi(r,t) = \frac{i}{\hbar}\mathbf{p}\psi(r,t) \qquad \text{or} \qquad \mathbf{p} \to \frac{\hbar}{i}\frac{\partial}{\partial \mathbf{r}} = \frac{\hbar}{i}\nabla$$

$$\nabla^2\psi(\mathbf{r},t) = \nabla\cdot(\nabla\psi)$$
$$= \left(\frac{i}{\hbar}\right)^2 \mathbf{p}\cdot\mathbf{p}\,\psi(\mathbf{r},t)$$
$$= -\frac{1}{\hbar^2}\mathbf{p}^2\psi(\mathbf{r},t) = -\frac{2m}{\hbar^2}E\psi(\mathbf{r},t) = -\frac{2m}{\hbar^2}i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t)$$

or

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r},t)$$

where the Laplacian operator is defined by

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

This is the time-dependent Schrödinger equation for free particle with mass *m*.

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) = H\psi(\mathbf{r},t)$$

where

$$H = \frac{\mathbf{p}^2}{2m} \qquad \text{and} \qquad \mathbf{p} \to \frac{\hbar}{i}\frac{\partial}{\partial \mathbf{r}} = \frac{\hbar}{i}\nabla$$

More generally, we have

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) = H\psi(\mathbf{r},t)$$

with the Hamiltonian given by

$$H = \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) \qquad \text{and} \qquad \mathbf{p} \to \frac{\hbar}{i}\frac{\partial}{\partial \mathbf{r}} = \frac{\hbar}{i}\nabla$$

for a particle in the presence of a potential $V(\mathbf{r})$.

2. Born's interpretation: probability

The currently held view connects the wavefunction with *probabilities* in the manner first proposed by Max Born in 1925:

(i) The quantum state of a particle is characterized by a wave function, $\psi(\mathbf{r},t)$.

(ii) $|\psi(\mathbf{r},t)|^2$ is a probability amplitude of the particle's.

$$dP(\mathbf{r},t) = |\psi(\mathbf{r},t)|^2 d\mathbf{r} = \psi^*(\mathbf{r},t)\psi(\mathbf{r},t)d\mathbf{r}$$

Probability of the particle being, at time *t* and in a volume element d***r*** = *dxdydz* situated at the point ***r***.

$$\int |\psi(\mathbf{r},t)|^2 d\mathbf{r} = 1 \qquad (1)$$

Set of square-integrable function where Eq.(1) converges. This set is called L^2 and has the structure of Hilbert space.

The probability of finding the particle in any finite volume *V* is given by

$$P = \int_V |\psi(\mathbf{r},t)|^2 d\mathbf{r}$$

((Note)) For the one dimensional case.
The probability of finding a particle for $a \le x \le b$ is given by\

$$\int_a^b |\psi(x,t)|^2 dx$$

If, at the instant time t, a measurement is made to locate the particle associated with the wave function $\psi(x,t)$, then the probability $P(x, t)$ that the particle will be found at a coordinate between x and $x + dx$ is equal to $\psi^*(x,t)\psi(x,t)dx$

3. Stationary states

We solve the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) = H\psi(\mathbf{r},t) = [-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})]\psi(\mathbf{r},t)$$

by using the method of separation variable, where the potential energy is independent of time. To this end, we assume that

$$\psi(\mathbf{r},t) = \varphi(\mathbf{r})T(t).$$

Then we have

$$i\hbar\varphi(\mathbf{r})\frac{\partial}{\partial t}T(t) = H\varphi(\mathbf{r})T(t)$$

or

$$i\hbar \frac{\frac{\partial}{\partial t}T(t)}{T(t)} = \frac{H\varphi(\mathbf{r})}{\varphi(\mathbf{r})} = E$$

The left side is a function of *t* alone, and the right side is a function of ***r*** alone. The only way this can possibly be true are in fact constant. The constant is assumed to be *E*, independent of *t* and ***r***.

$$i\hbar \frac{\partial}{\partial t}T(t) = ET(t)$$

$$H\psi(\mathbf{r}) = [-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \qquad \text{(eigenvalue problem)}$$

Thus

$$T(t) = \exp(-\frac{i}{\hbar}Et)$$

or

$$\psi(\mathbf{r},t) = \psi(\mathbf{r})\exp(-\frac{i}{\hbar}Et)$$

Therefore we have

$$|\psi(\mathbf{r},t)|^2 = |\psi(\mathbf{r})|^2$$

4. Current equation for the probability density

Probability density is defined as

$$\rho(\mathbf{r},t) = |\psi(\mathbf{r},t)|^2$$

Probability current density is given by

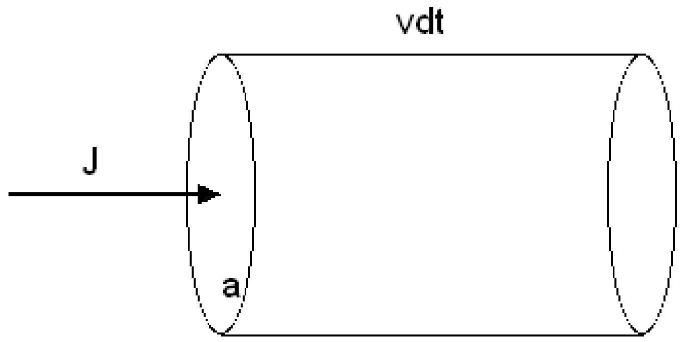
$$\mathbf{J} = \frac{\hbar}{2mi}[\psi^*(\mathbf{r},t)\nabla\psi(\mathbf{r},t) - \psi(\mathbf{r},t)\nabla\psi^*(\mathbf{r},t)]$$

Equation of continuity equation:

$$\frac{\partial}{\partial t}\rho(\mathbf{r},t) + \nabla\cdot\mathbf{j}(r,t) = 0$$

which is analogues to the classical equation of continuity.

((Note))



J: particles number flowing per unit area per unit time.

$$Jadt = |\psi|^2 avdt$$

or

$$J = |\psi|^2 v = \frac{p}{m}|\psi|^2$$

(a) Suppose that

$$\psi(r,t) = C\exp[\frac{i}{\hbar}(\mathbf{p}\cdot\mathbf{r} - Et)] = C\exp[-\frac{i}{\hbar}Et]\varphi(\mathbf{r})$$

The probability current density is

$$\begin{aligned}
\mathbf{J} &= \frac{\hbar}{2mi}[\varphi^*(\mathbf{r})\nabla\varphi(\mathbf{r}) - \varphi(\mathbf{r})\nabla\varphi(\mathbf{r})] \\
&= \frac{\hbar}{2mi}[C^*\exp(-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r})C(\frac{i\mathbf{p}}{\hbar})\exp(\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r})] \\
&= \frac{\hbar}{2mi}[-C^*(-\frac{i\mathbf{p}}{\hbar})\exp(-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r})C\exp(\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r})] \\
&= \frac{\mathbf{p}}{m}|C|^2 = v|\psi|^2
\end{aligned}$$

(b) Suppose that the wave is given by the superposition

$$\psi(r,t) = A\exp[\frac{i}{\hbar}(\mathbf{p}\cdot\mathbf{r} - Et)] + B\exp[-\frac{i}{\hbar}(\mathbf{p}\cdot\mathbf{r} + Et)]$$
$$= \exp(-\frac{i}{\hbar}Et)[A\exp(\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}) + B\exp(-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r})]$$
$$= \exp(-\frac{i}{\hbar}Et)\varphi(\mathbf{r})$$

The complex conjugate of $\psi(r,t)$ is given by

$$\psi^*(\mathbf{r},t) = \exp(\frac{i}{\hbar}Et)\varphi^8(\mathbf{r})$$

where

$$\varphi(\mathbf{r}) = A\exp(\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}) + B\exp(-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r})$$

Then the probability current density is

$$\mathbf{J} = \frac{\hbar}{2mi}[\varphi^*(\mathbf{r})\nabla\varphi(\mathbf{r}) - \varphi(\mathbf{r})\nabla\varphi(\mathbf{r})]$$
$$=$$
$$= \frac{\hbar}{2mi}[\{A^*\exp(-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}) + B^*\exp(\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r})]\}\{A(\frac{i\mathbf{p}}{\hbar})\exp(\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r})$$
$$+ B(\frac{-i\mathbf{p}}{\hbar})\exp(-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r})]\} - \{A\exp(\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}) + B\exp(-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r})]\}$$
$$\times\{A^*(-\frac{i\mathbf{p}}{\hbar})\exp(-\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r}) + B^*(\frac{i\mathbf{p}}{\hbar})\exp(\frac{i}{\hbar}\mathbf{p}\cdot\mathbf{r})]\}$$
$$= \frac{\hbar}{2mi}[2(A^*A\frac{i\mathbf{p}}{\hbar} - B^*B\frac{i\mathbf{p}}{\hbar})$$
$$= \frac{\mathbf{p}}{m}(A^*A - B^*B)$$
$$= \frac{\mathbf{p}}{m}(|A|^2 - |B|^2)$$

5. Derivation of the expression for the current density; general case

Probability density:

$$\rho(\mathbf{r},t) = |\psi(\mathbf{r},t)|^2$$

The integral;

$$\int \left|\psi(\mathbf{r},t)\right|^2 d\mathbf{r}$$

taken over some finite volume *V*, is the probability of finding the particle in this volume. Let us calculate the derivative of the probability with respect to time *t*.

$$\frac{\partial}{\partial t}\int \left|\psi(\mathbf{r},t)\right|^2 d\mathbf{r} = \int (\frac{\partial \psi^*}{\partial t}\psi + \psi^* \frac{\partial \psi}{\partial t})d\mathbf{r} = -\frac{1}{i\hbar}\int [(H^*\psi^*)\psi - \psi^*(H\psi)]d\mathbf{r}$$

Here

$$i\hbar\frac{\partial \psi}{\partial t} = H\psi$$

Complex conjugate of this equation:

$$-i\hbar\frac{\partial \psi^*}{\partial t} = H^*\psi^* = H\psi^*$$

where *H* is the Hamiltonian,

$$H^* = H = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$$

Then we get

$$\begin{aligned}(H^*\psi^*)\psi - \psi^*(H\psi) &= (H\psi^*)\psi - \psi^*(H\psi) \\ &= \{[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})]\psi^*\}\psi - \psi^*\{[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})]\psi\} \\ &= -\frac{\hbar^2}{2m}[(\nabla^2\psi^*)\psi - \psi^*(\nabla^2\psi)]\end{aligned}$$

Using the Green's theorem (see below), we have

$$\begin{aligned}\frac{\partial}{\partial t}\int \left|\psi(\mathbf{r},t)\right|^2 d\mathbf{r} &= \frac{\hbar}{2mi}\int [(\nabla^2\psi^*)\psi - \psi^*(\nabla^2\psi)]d\mathbf{r} \\ &= \int (\nabla\cdot\mathbf{J})d\mathbf{r} = \int \mathbf{J}\cdot d\mathbf{a}\end{aligned}$$

Note that the current density is defined as

$$\mathbf{J} = \frac{\hbar}{2mi}[\psi^*\nabla\psi - \psi\nabla\psi^*]$$

and

$$\nabla\cdot\mathbf{J}=\frac{\hbar}{2mi}[(\nabla^2\psi^*)\psi-\psi^*(\nabla^2\psi)]=\nabla\cdot\frac{\hbar}{2mi}(\psi\nabla\psi^*-\psi^*\nabla\psi)$$

Finally we have the equation of continuity

$$\int\frac{\partial}{\partial t}\rho d\mathbf{r}=-\int\nabla\cdot\mathbf{J}d\mathbf{r}=-\int\mathbf{J}\cdot d\mathbf{a}\ \text{(Gauss's theorem)}$$

or

$$\frac{\partial}{\partial t}\rho+\nabla\cdot\mathbf{j}=0 \qquad \text{(equation of continuity)}$$

6. Green's theorem

$$\int_V(\psi\nabla^2\phi-\phi\nabla^2\psi)d\tau=\int_S(\psi\nabla\phi-\phi\nabla\psi)\cdot d\mathbf{a}$$

((Proof)) In the Gauss's theorem, we put

$$\mathbf{A}=\psi\nabla\phi$$

Then we have

$$I_1=\int_V\nabla\cdot\mathbf{A}d\tau=\int_V\nabla\cdot(\psi\nabla\phi)d\tau=\int_S(\psi\nabla\phi)\cdot d\mathbf{a}$$

Noting that

$$\nabla\cdot(\psi\nabla\phi)=\psi\nabla^2\phi+\nabla\psi\cdot\nabla\phi$$

we have

$$I_1=\int_V(\psi\nabla^2\phi+\nabla\psi\cdot\nabla\phi)d\tau=\int_S(\psi\nabla\phi)\cdot d\mathbf{a}$$

By replacing $\psi\leftrightarrow\phi$, we also have

$$I_1=\int_V(\phi\nabla^2\psi+\nabla\phi\cdot\nabla\psi)d\tau=\int_S(\phi\nabla\psi)\cdot d\mathbf{a}$$

Thus we find the Green's theorem

$$I_1 - I_2 = \int_V (\psi\nabla^2\phi - \phi\nabla^2\psi)d\tau = \int_S (\psi\nabla\phi - \phi\nabla\psi)\cdot d\mathbf{a}$$

7. The mean value of position for the stationary states

In the stationary state, the wave function itself

$$\psi(x,t) = \psi(x)\exp(-\frac{i}{\hbar}Et)$$

depends on *t*, but the probability density

$$\psi^*(x,t)\psi(x,t) = \psi^*(x)\exp(\frac{i}{\hbar}Et)\psi(x)\exp(-\frac{i}{\hbar}Et)$$
$$= |\psi(x)|^2$$

does not depend on *t*.

A single measurement yields the result that the particle is to be found in the interval *x* – *x* + d*x*. The corresponding probability is

$$|\psi(x)|^2 dx$$

The mean value of the position *x* is defined as

$$\langle x \rangle = \int_{-\infty}^{\infty} x|\psi(x)|^2 dx$$

where

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

Correspondingly, the mean value of the *n*-th power of *x*, x^n, is obtained as

$$\langle x^n \rangle = \int_{-\infty}^{\infty} x^n|\psi(x)|^2 dx$$

If the function x^n is replaced by the potential energy *V*(*x*), the mean value of the potential energy is obtained as

$$\langle V(x) \rangle = \int_{-\infty}^{\infty} V(x)|\psi(x)|^2 dx$$

The fluctuation is defined by

$$\left\langle (x-\langle x\rangle)^2 \right\rangle = \int_{-\infty}^{\infty} (x-\langle x\rangle)^2 |\psi(x)|^2 dx$$
$$= \int_{-\infty}^{\infty} (x^2 - 2\langle x\rangle x + \langle x\rangle^2) |\psi(x)|^2 dx$$
$$= \left\langle x^2 \right\rangle - \langle x\rangle^2$$

8. The mean value of momentum

The mean value of the momentum *p* is defined as

$$\langle p\rangle = \int_{-\infty}^{\infty} \psi^*(x) \frac{\hbar}{i} \frac{\partial}{\partial x} \psi(x) dx$$

Correspondingly, the mean value of the *n*-th power of *p*, p^n, is obtained as

$$\left\langle p^n \right\rangle = \int_{-\infty}^{\infty} \psi^*(x) \left(\frac{\hbar}{i} \frac{\partial}{\partial x}\right)^n \psi(x) dx$$

9. Fourier transform of $\psi(x)$

From the definition, the Fourier transform of $\psi(x)$ can be expressed by

$$\psi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int \exp(-\frac{i}{\hbar} px) \psi(x) dx$$

The inverse Fourier transform is given by

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int \exp(\frac{i}{\hbar} px) \psi(p) dp \ .$$

Noting that

$$\psi^*(x) \frac{\hbar}{i} \frac{\partial}{\partial x} \psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int \exp(-\frac{i}{\hbar} p'x) \psi^*(p') dp' \frac{1}{\sqrt{2\pi\hbar}} \frac{\hbar}{i} \frac{\partial}{\partial x} \int \exp(\frac{i}{\hbar} p''x) \psi(p'') dp''$$
$$= \frac{1}{2\pi\hbar} \iint \exp(-\frac{i}{\hbar} p'x) \psi^*(p') \frac{\hbar}{i} \frac{i}{\hbar} p'' \exp(\frac{i}{\hbar} p''x) \psi(p'') dp' dp''$$
$$= \frac{1}{2\pi\hbar} \iint dp' dp'' p'' \exp(-\frac{i}{\hbar} (p'-p'')x] \psi^*(p') \psi(p'')$$

we have

$$\int \psi^*(x)\frac{\hbar}{i}\frac{\partial}{\partial x}\psi(x)dx = \frac{1}{2\pi\hbar}\iint dp'\,dp''\,p''\psi^*(p')\psi(p'')\int \exp(-\frac{i}{\hbar}(p'-p'')x]dx$$
$$= \frac{1}{2\pi\hbar}\iint dp'\,dp''\,p''\psi^*(p')\psi(p'')2\pi\delta[\frac{1}{\hbar}(p'-p'')]$$
$$= \iint dp'\,dp''\,p''\psi^*(p')\psi(p'')\delta[p'-p'']$$
$$= \int dp'\,p'\psi^*(p')\psi(p')$$

Here we use the property of the delta function;

$$\int \exp(-\frac{i}{\hbar}px)dx = 2\pi\hbar\delta(p-p')$$

Then the average value of the momentum can be expressed by

$$\langle p\rangle = \int_{-\infty}^{\infty} p\psi^*(p)\psi(p)dp$$

Correspondingly, the mean value of the *n*-th power of *p*, p^n, is obtained as

$$\langle p^n\rangle = \int_{-\infty}^{\infty} p^n\psi^*(p)\psi(p)dp$$

We note that

$$\langle x\rangle = \int_{-\infty}^{\infty} \psi^*(p)i\hbar\frac{\partial}{\partial p}\psi(p)dp$$

since

$$\psi^*(p)i\hbar\frac{\partial}{\partial p}\psi(p) = \frac{1}{\sqrt{2\pi\hbar}}\int \exp(\frac{i}{\hbar}px')\psi^*(x')dx'\frac{1}{\sqrt{2\pi\hbar}}i\hbar\frac{\partial}{\partial p}\int \exp(-\frac{i}{\hbar}px'')\psi(x'')dx''$$
$$= \frac{1}{2\pi\hbar}\iint \exp(\frac{i}{\hbar}px')\psi^*(x')i\hbar(-\frac{i}{\hbar})x''\exp(-\frac{i}{\hbar}px'')\psi(x'')dx'dx''$$
$$= \frac{1}{2\pi\hbar}\iint dx'\,dx''\,x''\exp[\frac{i}{\hbar}(x'-x'')p]\psi^*(x')\psi(x'')$$

we have

$$\int \psi^*(p) i\hbar \frac{\partial}{\partial p}\psi(p)dp = \frac{1}{2\pi\hbar}\iint dx' dx'' x'' \psi^*(x')\psi(x'')\int \exp(\frac{i}{\hbar}(x'-x'')p]dp$$
$$= \frac{1}{2\pi\hbar}\iint dx' dx'' x'' \psi^*(x')\psi(x'') 2\pi\delta[\frac{1}{\hbar}(x'-x'')]$$
$$= \iint dx' dx'' x'' \psi^*(x')\psi(x'')\delta[x'-x'']$$
$$= \int dx' x' \psi^*(x')\psi(x')$$
$$= \langle x \rangle$$

where $x \to i\hbar \frac{\partial}{\partial p}$.

APPENDIX

((**Mathematica**)) **Vector Analysis Cartesian**

Probability current density: we assume that the amplitude of the plane wave is real. for simpicity

```
Clear["Gobal`"]; Needs["VectorAnalysis`"];
SetCoordinates[Cartesian[x, y, z]];
```

```
K1 =
  -ℏ/(2 ⅈ m) (Grad[ψ1[x, y, z]] ψ[x, y, z] -
     ψ1[x, y, z] Grad[ψ[x, y, z]]);
```

```
rule1 =
  {ψ1 →
    (Exp[-ⅈ/ℏ ϵ t]
       (A0 Exp[ⅈ/ℏ (px #1 + py #2 + pz #3)] +
         A1 Exp[-ⅈ/ℏ (px #1 + py #2 + pz #3)]) &)};
```

```
rule2 =
  {ψ →
    (Exp[ⅈ/ℏ ϵ t] (A0 Exp[-ⅈ/ℏ (px #1 + py #2 + pz #3)] +
         A1 Exp[ⅈ/ℏ (px #1 + py #2 + pz #3)]) &)};
```

```
J = K1 /. rule1 /. rule2 // Simplify
```

$$\left\{\frac{\left(-A0^2+A1^2\right)\,px}{m},\ \frac{\left(-A0^2+A1^2\right)\,py}{m},\ \frac{\left(-A0^2+A1^2\right)\,pz}{m}\right\}$$