

Lecture notes: QM 01

The Schrödinger equation

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1 Operator

The wave function or de Broglie wave for a free particle with momentum p and energy E is given by

$$\Psi(x, t) = e^{i(kx - \omega t)}, \quad (1)$$

where ω and k are determined from

$$p = \hbar k, \quad E = \hbar \omega, \quad E = \frac{p^2}{2m}.$$

The wave function (1) represents a state of definite momentum and is also written as

$$\Psi(x, t) = e^{i(px - Et)/\hbar}. \quad (2)$$

Since the wave function contains all the information about the system, it is often of interest to find appropriate operators to extract information from the wave function. To extract the value of momentum from the wave function (1) or (2) we need an operator

which must be, roughly, a derivative with respect to x . In fact we take

$$\begin{aligned}
\frac{\hbar}{i} \frac{\partial}{\partial x} \Psi(x, t) &= \frac{\hbar}{i} \frac{\partial}{\partial x} e^{i(kx - \omega t)} \\
&= \frac{\hbar}{i} (ik) e^{i(kx - \omega t)} \\
&= \frac{\hbar}{i} (ik) \Psi(x, t) \\
&= \hbar k \Psi(x, t) \\
&= p \Psi(x, t)
\end{aligned} \tag{3}$$

where the p factor in the right-hand side is just the momentum. We thus identify the operator $\frac{\hbar}{i} \frac{\partial}{\partial x}$ as the **momentum operator** \hat{p}

$$\boxed{\hat{p} \equiv \frac{\hbar}{i} \frac{\partial}{\partial x} = -i\hbar \frac{\partial}{\partial x}} \tag{4}$$

and we have verified that acting on the wave function $\Psi(x, t)$ for a particle of momentum p it gives p times the wave function:

$$\hat{p} \Psi(x, t) = -i\hbar \frac{\partial}{\partial x} \Psi(x, t) = p \Psi(x, t). \tag{5}$$

The momentum operator acts on wave functions, which are functions of space and time to give another function of space and time. Since \hat{p} acting on $\Psi(x, t)$ gives a number (p , in fact) times $\Psi(x, t)$ we say that $\Psi(x, t)$ is an **eigenstate** of \hat{p} . The matrix algebra analogy is useful: matrices are the operators and column vectors are the states. Matrices act by multiplication on column vectors. An eigenvector of a matrix is a special vector. The matrix acting on an eigenvector gives a number times the eigenvector. After the action of the matrix the direction of the vector is unchanged but its magnitude can be scaled. The same for eigenstates of operators: an operator acting on an eigenstate gives the eigenstate up to a multiplicative constant. We also say that $\Psi(x, t)$ is a state of **definite momentum**.

Let us now consider extracting the energy information from the free particle wave function. This time we must avail ourselves of the time derivative:

$$\begin{aligned}
i\hbar \frac{\partial}{\partial t} \Psi(x, t) &= i\hbar \frac{\partial}{\partial t} e^{i(kx - \omega t)} \\
&= i\hbar (-i\omega) e^{i(kx - \omega t)} \\
&= i\hbar (-i\omega) \Psi(x, t) \\
&= \hbar \omega \Psi(x, t) \\
&= E \Psi(x, t).
\end{aligned} \tag{6}$$

Hence we define the total energy operator \hat{E} such that

$$\boxed{\hat{E} = i\hbar \frac{\partial}{\partial t}} \tag{7}$$

Now, for a free particle the total energy is the kinetic energy and is given in terms of momentum such that

$$E = \frac{p^2}{2m}. \quad (8)$$

We can use (8) to construct the relevant energy operator (which is the kinetic energy for a free particle) in terms of the momentum. By using (8) on the right-hand side of (6) we write

$$E\Psi = \frac{p^2}{2m}\Psi = \frac{p}{2m}p\Psi = \frac{p}{2m}\hat{p}\Psi = \frac{p}{2m}(-i\hbar)\frac{\partial}{\partial x}\Psi \quad (9)$$

where we used (5) to write $p\Psi$ as the momentum operator acting on Ψ . Since p is a constant we can move the p factor on the last right-hand side close to the wave function and then replace it by the momentum operator:

$$\begin{aligned} E\Psi &= \frac{1}{2m}(-i\hbar)\frac{\partial}{\partial x}p\Psi \\ &= \frac{1}{2m}(-i\hbar)\frac{\partial}{\partial x}(-i\hbar)\frac{\partial}{\partial x}\Psi \\ &= -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}. \end{aligned} \quad (10)$$

This can also be written as

$$E\Psi = \frac{1}{2m}\hat{p}\hat{p}\Psi = \frac{\hat{p}^2}{2m}\Psi, \quad (11)$$

which suggests the following definition of the energy operator (for a free particle):

$$\hat{E} \equiv \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}. \quad (12)$$

For the free particle wave function (1) we show that

$$\begin{aligned} \hat{E}\Psi(x, t) &= -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x, t)}{\partial x^2} \\ &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}e^{i(kx-\omega t)} \\ &= -\frac{\hbar^2}{2m}(ik)^2e^{i(kx-\omega t)} \\ &= \frac{\hbar^2k^2}{2m}\Psi(x, t) \\ &= \frac{p^2}{2m}\Psi(x, t) \\ &= E\Psi(x, t) \end{aligned} \quad (13)$$

To be more precise (12) is the kinetic energy operator and to be written as

$$\boxed{\hat{T} \equiv -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}.} \quad (14)$$

Suppose now that our quantum particle is not free but rather is moving in some external potential $V(x, t)$. In this case, the total energy of the particle is no longer simply kinetic, it is the sum of kinetic and potential energies:

$$E = \frac{p^2}{2m} + V(x, t). \quad (15)$$

This naturally suggests that the total energy operator should take the form

$$\begin{aligned} \hat{E} &= \frac{\hat{p}^2}{2m} + V(x, t) \\ &= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t). \end{aligned} \quad (16)$$

The first term, as we already know, involves second derivatives with respect to x . The second term acts multiplicatively: acting on any wave function $\Psi(x, t)$ it simply multiplies it by $V(x, t)$.

At this point, we introduce another very important operator: the **position operator** \hat{x} that acting on functions of x gives another function of x as follows:

$$\hat{x}f(x) \equiv xf(x). \quad (17)$$

Note that it follows from this equation and successive applications of it that

$$\hat{x}^k f(x) \equiv x^k f(x). \quad (18)$$

If the potential $V(x, t)$ can be written as some series expansion in terms of x it then follows that

$$V(\hat{x}, t)\Psi(x, t) \equiv V(x, t)\Psi(x, t). \quad (19)$$

The operators we are dealing with (momentum, position, Hamiltonian) are all declared to be linear operators. A **linear operator** \hat{A} satisfies

$$\hat{A}(a\phi) \equiv a\hat{A}\phi, \quad \hat{A}(\phi_1 + \phi_2) \equiv \hat{A}\phi_1 + \hat{A}\phi_2 \quad (20)$$

where a is a constant. Two linear operators \hat{A} and \hat{B} that act on the same set of objects can always be added

$$(\hat{A} + \hat{B})\phi \equiv \hat{A}\phi + \hat{B}\phi. \quad (21)$$

They can also be multiplied, the product $\hat{A}\hat{B}$ is a linear operator defined by

$$\hat{A}\hat{B}\phi \equiv \hat{A}(\hat{B}\phi), \quad (22)$$

meaning that you act first with \hat{B} , which is closest to ϕ and then act on the result with \hat{A} . The order of multiplication matters and thus $\hat{A}\hat{B}$ and $\hat{B}\hat{A}$ may not be the same operators.

2 Commutator

The commutator of two operators \hat{A} and \hat{B} , denoted by $[\hat{A}, \hat{B}]$, is defined by

$$\boxed{[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A}}, \quad (23)$$

and the anticommutator $\{\hat{A}, \hat{B}\}$ is defined by

$$\boxed{\{\hat{A}, \hat{B}\} \equiv \hat{A}\hat{B} + \hat{B}\hat{A}}. \quad (24)$$

Two operators are said to commute if their commutator is equal to zero and hence $\hat{A}\hat{B} = \hat{B}\hat{A}$. Any operator commutes with itself:

$$[\hat{A}, \hat{A}] = 0 \quad (25)$$

The commutator also satisfies the following properties:

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

$$[\hat{A}, \hat{B} + \hat{C}] = [\hat{A}, \hat{B}] + [\hat{A}, \hat{C}] \quad (26)$$

$$[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}] \quad (27)$$

$$[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B} \quad (28)$$

$$0 = [\hat{A}, [\hat{B}, \hat{C}]] + [\hat{B}, [\hat{C}, \hat{A}]] + [\hat{C}, [\hat{A}, \hat{B}]]. \quad (29)$$

We have operators \hat{x} and \hat{p} that are clearly somewhat related. We would like to know their commutator $[\hat{x}, \hat{p}]$. For this we let $[\hat{x}, \hat{p}]$ act on some arbitrary function $\phi(x)$ and then attempt simplification.

$$\begin{aligned} [\hat{x}, \hat{p}]\phi(x) &= (\hat{x}\hat{p} - \hat{p}\hat{x})\phi(x) \\ &= \hat{x}\hat{p}\phi(x) - \hat{p}\hat{x}\phi(x) \\ &= \hat{x}(\hat{p}\phi(x)) - \hat{p}(\hat{x}\phi(x)) \\ &= \hat{x}\left(-i\hbar\frac{\partial\phi(x)}{\partial x}\right) - \hat{p}(x\phi(x)) \\ &= -i\hbar x\frac{\partial\phi(x)}{\partial x} + i\hbar\frac{\partial}{\partial x}(x\phi(x)) \\ &= -i\hbar x\frac{\partial\phi(x)}{\partial x} + i\hbar x\frac{\partial\phi(x)}{\partial x} + i\hbar\phi(x) \\ &= i\hbar\phi(x), \end{aligned} \quad (30)$$

so that, all in all, we have shown that for arbitrary $\phi(x)$ one has

$$[\hat{x}, \hat{p}]\phi(x) = i\hbar\phi(x). \quad (31)$$

Since this equation holds for any $\phi(x)$ it really represents the equality of two operators. Whenever $\hat{A}\phi(x) = \hat{B}\phi(x)$ for arbitrary $\phi(x)$ we simply say that $\hat{A} = \hat{B}$. The operators are the same because they give the same result acting on anything! We have therefore discovered the most fundamental commutation relation in quantum mechanics:

$$\boxed{[\hat{x}, \hat{p}] = i\hbar}. \quad (32)$$

The right hand side is a number, but should be viewed as an operator (acting on any function it multiplies by the number). This commutation relation can be used to prove Heisenbergs uncertainty principle, which states that the product of the position uncertainty and the momentum uncertainty must always exceed $\hbar/2$.

The idea that operators can fail to commute may remind you of matrix multiplication, which is also non-commutative. We thus have the following correspondences:

$$\begin{aligned} \text{operators} &\leftrightarrow \text{matrices} \\ \text{wave functions} &\leftrightarrow \text{vectors} \\ \text{eigenstates} &\leftrightarrow \text{eigenvectors} \end{aligned} \tag{33}$$

One can in fact formulate Quantum Mechanics using matrices, so these correspondences are actually concrete and workable.

As an example of useful matrices that do not commute, consider the Pauli matrices, three two-by-two matrices given by

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{34}$$

Actually these matrices are exactly what is needed to consider spin one-half particles. The spin operator \mathbf{S} has three components $S_i = \frac{\hbar}{2}\sigma_i$. Let us now see if σ_1 and σ_2 commute.

$$\begin{aligned} \sigma_1\sigma_2 &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} \\ \sigma_2\sigma_1 &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} \end{aligned}$$

Therefore

$$[\sigma_1, \sigma_2] = \begin{pmatrix} 2i & 0 \\ 0 & -2i \end{pmatrix} = 2i \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = 2i\sigma_3. \tag{35}$$

In fact, one can also show that

$$[\sigma_2, \sigma_3] = 2i\sigma_1 \quad [\sigma_3, \sigma_1] = 2i\sigma_2. \tag{36}$$

Matrix mechanics was worked out in 1925 by Werner Heisenberg and clarified by Max Born and Pascual Jordan. Note that, if we were to write \hat{x} and \hat{p} operators in matrix form, they would require infinite dimensional matrices. One can show that there are no finite size matrices that commute to give a number times the identity matrix, as is required from (32). This should not surprise us: on the real line there are an infinite number of linearly independent wave functions, and in view of the correspondences in (33) it would suggest an infinite number of basis vectors. The relevant matrices must therefore be infinite dimensional.

For three dimension just like we defined a position operator \hat{x} , we now have three position operators $(\hat{x}, \hat{y}, \hat{z})$ making up $\hat{\mathbf{r}}$, that is

$$\hat{\mathbf{r}} \equiv (\hat{x}, \hat{y}, \hat{z}) \tag{37}$$

Similarly for three dimension we define the momentum operator $\hat{\mathbf{p}}$ as follows:

$$\hat{\mathbf{p}} \equiv -i\hbar\nabla \quad (38)$$

where $\nabla = (\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z})$ is the gradient operator. If we call the momentum components $(p_1, p_2, p_3) = (p_x, p_y, p_z)$ and the coordinates as $(x_1, x_2, x_3) = (x, y, z)$ then we have that the components of the above equation are

$$\hat{p}_k = -i\hbar \frac{\partial}{\partial x_k}, \quad k = 1, 2, 3. \quad (39)$$

With three position and three momentum operators, we now should state the nine possible commutation relations. If you recall our derivation of $[\hat{x}, \hat{p}] = i\hbar$ you will note that the commutator vanishes unless the subscripts on \hat{x} and \hat{p} are the same. This means that we have

$$[\hat{x}_i, \hat{p}_j] = i\hbar \delta_{ij}, \quad (40)$$

where the Kronecker delta is defined by

$$\delta_{ij} = \begin{cases} 1 & \text{if } i = j, \\ 0 & \text{if } i \neq j. \end{cases} \quad (41)$$

In a nutshell for the components of $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ we have

$$\boxed{[\hat{x}, \hat{p}_x] = [\hat{y}, \hat{p}_y] = [\hat{z}, \hat{p}_z] = i\hbar} \quad (42)$$

and

$$\boxed{[\hat{x}, \hat{p}_y] = [\hat{x}, \hat{p}_z] = [\hat{y}, \hat{p}_x] = [\hat{y}, \hat{p}_z] = [\hat{z}, \hat{p}_x] = [\hat{z}, \hat{p}_y] = 0} \quad (43)$$

3 The Schrödinger equation

Let us consider the free particle and find a differential equation for which the de Broglie wave function (1) is a solution. Consider (6) and using (10) for the right-hand side we have

$$\boxed{i\hbar \frac{\partial}{\partial t} \Psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x, t).} \quad (44)$$

This is the free-particle Schrödinger equation. More schematically, using the energy operator, it can be written as

$$\boxed{i\hbar \frac{\partial}{\partial t} \Psi(x, t) = \hat{E} \Psi(x, t).} \quad (45)$$

It is worth re-checking that our de Broglie wave function satisfies the Schrödinger equation (44). Indeed for $\Psi(x, t) = e^{i(kx - \omega t)}$ we find

$$i\hbar(-i\omega)\Psi = -\frac{\hbar^2}{2m}(ik)^2\Psi \quad (46)$$

which is a solution since the Ψ factors cancel and all that is needed is the equality

$$\hbar\omega = \frac{\hbar^2 k^2}{2m}, \quad (47)$$

which is recognized as the familiar relation $E = p^2/(2m)$.

In case of a particle in a potential $V(x, t)$ we take the form (45) and replace \hat{E} by the energy operator in (16) to postulate the Schrödinger equation as

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t) \right) \Psi(x, t). \quad (48)$$

The energy operator \hat{E} is usually called the Hamiltonian operator \hat{H} , so one has

$$\hat{H} \equiv -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t), \quad (49)$$

and the Schrödinger equation takes the form

$$i\hbar \frac{\partial}{\partial t} \Psi(x, t) = \hat{H} \Psi(x, t). \quad (50)$$

The Schrödinger equation has an explicit i on the left-hand side. This i shows that it is impossible to find a solution for real Ψ . If Ψ were real the right-hand side of the equation would be real but the left-hand side would be imaginary. Thus, the Schrödinger equation forces us to work with complex wave functions.

Note also that the Schrödinger equation does not take the form of a conventional wave equation. A conventional wave equation for a variable ϕ takes the form

$$\frac{\partial^2 \phi}{\partial x^2} - \frac{1}{V^2} \frac{\partial^2 \phi}{\partial t^2} = 0. \quad (51)$$

The general solutions of this linear equation are $f_{\pm}(x \pm Vt)$. This would certainly allow for real solutions, which are not acceptable in quantum theory. The Schrödinger equation has no second-order time derivatives. It is first-order in time!

Two basic properties of the Schrödinger equation:

- The differential equation is first order in time. This means that for an initial condition it suffices to know the wave function completely at some initial time t_0 and the Schrödinger equation then determines the wave function for all times. This can be understood very explicitly. If we know $\Psi(x, t_0)$ for all x then the right-hand side of the Schrödinger equation, which just involves x derivatives and multiplication, can be evaluated at any point x . This means that at any point x we know the time-derivative of the wave function (left-hand side of the Schrödinger equation) and this allows us to calculate the wave function a little time later.

- Linearity and superposition. The Schrödinger equation is a linear equation for complex wave functions. Therefore, given two solutions Ψ_1 and Ψ_2 , we can form new solutions as linear combinations $\alpha\Psi_1 + \beta\Psi_2$ with complex coefficients α and β .

We have written the Schrödinger equation for a particle on a one-dimensional potential. In order to write now the general Schrödinger equation we need to consider the Hamiltonian operator:

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + V(\mathbf{r}, t). \quad (52)$$

This time

$$\hat{\mathbf{p}}^2 = \hat{\mathbf{p}} \cdot \hat{\mathbf{p}} = (-i\hbar\nabla) \cdot (-i\hbar\nabla) = -\hbar^2 \nabla^2 \quad (53)$$

where ∇^2 is the Laplacian operator

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \quad (54)$$

The Schrödinger equation finally takes the form

$$\boxed{i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t) \right) \Psi(\mathbf{r}, t).} \quad (55)$$

4 Interpreting the wave function

Schrödinger thought that the wave function Ψ represents a particle that could spread out and disintegrate. The fraction of the particle to be found at x would be proportional to the magnitude of $|\Psi|^2$. This was problematic, as noted by Max Born (1882-1970). Born solved the Schrödinger equation for scattering of a particle in a potential, finding a wave function that fell like $1/r$, with r the distance to the scattering center. But Born also noticed that in the experiment one does not find fractions of particles going in many directions but rather particles remain whole. Born suggested a probabilistic interpretation. In his proposal,

The wave function $\Psi(x, t)$ does not tell us how much of the particle is at position x at time t but rather the probability that upon measurement taken at time t we would find the particle at position x .

To make this precise we use an infinitesimal volume element with volume $d\mathbf{r} = dx dy dz$ centered around some arbitrary point \mathbf{r} . The probability dP to find the particle within the volume element $d\mathbf{r}$ at time t is

$$dP = |\Psi(\mathbf{r}, t)|^2 d\mathbf{r}. \quad (56)$$

Consistency requires that the total probability to find the particle somewhere in the whole space is unity. Thus the integral of dP over all of space must give one:

$$\int_{\text{all space}} |\Psi(\mathbf{r}, t)|^2 d\mathbf{r} = 1 \quad (57)$$

References

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