Physical Chemistry 2

Lecture 2. The Schrödinger Equation

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Topics in Lecture 2

Probability (discrete and continuous variables)

Calculation of mean values

Concept of wavefuntion

Schrödinger equation

In Atkins' *Physical Chemistry* (11th ed.),

7B Wavefunctions

Reference for this lecture

David J. Griffiths, Darrell F. Schroeter
Introduction to Quantum Mechanics (3rd ed.), Cambridge University Press (2018).

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Discrete variables

Suppose there exists: five 50 won coins, ten 100 won coins, and five 500 won coins (total 20).
If we let $N(j)$ represent the number of coins with value j, then

$$N(50) = 5, N(100) = 10, N(500) = 5 \quad \text{where} \quad N = \sum_j N(j) = 20$$

If one selected one coin among 20 coins, *probability* of picking a coin with value j is

$$P(j) = \frac{N(j)}{N}$$

Note that sum of all the probabilities is 1. We call this *normalization*: $\sum_j P(j) = 1$

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Discrete variables

Average or **Mean value** or **Expectation value**

The average value of j (which we shall write $\langle j \rangle$) is

$$\langle j \rangle = \frac{1}{N} \sum jN(j) = \sum_j jP(j)$$

Similarly, we can calculate the average of the *squares* of coin values.

$$\langle j^2 \rangle = \sum_j j^2 P(j)$$

Example. P(50)=0.25, P(100)=0.5, P(500)=0.25.

$$\langle j \rangle = 0.25 \times 50 + 0.5 \times 100 + 0.25 \times 500 = 187.5$$

$$\langle j^2 \rangle = 0.25 \times 50^2 + 0.5 \times 100^2 + 0.25 \times 500^2 = 68,125$$

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Discrete variables

However, average cannot tell us everything about the distribution. Therefore we need a measure of *spread* of the distribution: *variance* and *standard deviation*.

Variance is defined as the average of $(\Delta j)^2$ where $\Delta j = j - \langle j \rangle$, and standard deviation is a square root of variance. So

$$\sigma^2 = \left\langle (\Delta j)^2 \right\rangle = \sum_j (j - \langle j \rangle)^2 P(j) = \left\langle j^2 \right\rangle - \langle j \rangle^2$$

Example. P(50)=0.25, P(100)=0.5, P(500)=0.25.

$$\langle j \rangle = 0.25 \times 50 + 0.5 \times 100 + 0.25 \times 500 = 187.5$$

$$\left\langle j^2 \right\rangle = 0.25 \times 50^2 + 0.5 \times 100^2 + 0.25 \times 500^2 = 68,125$$

$$\sigma^2 = 68,125 - 187.5^2 = 32,968.75, \quad \sigma \simeq 181.6$$

Continuous variables

For continuous variables, *infinitesimal intervals* should be considered.

Probability that a continuous variable lies between *x* and *x+dx* is $\rho(x)\,dx$.

The factor $\rho(x)$ is called *probability density function*. Then probability for $a \leq x \leq b$ is

$$P(a \leq x \leq b) = \int_a^b \rho(x)\,dx$$

Formulae we deduced for discrete distributions holds in the same way.

$$\int_{-\infty}^{\infty} \rho(x)\,dx = 1$$

$$\langle x \rangle = \int_{-\infty}^{\infty} x\rho(x)\,dx, \quad \left\langle x^2 \right\rangle = \int_{-\infty}^{\infty} x^2\rho(x)\,dx$$

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Gaussian Integrals

Start from the basic gaussian function. Change the variables into polar coordinates.

$$\left(\int_{-\infty}^{\infty} e^{-ax^2} \, dx \right)^2 = \int_{-\infty}^{\infty} e^{-ax^2} \, dx \int_{-\infty}^{\infty} e^{-ay^2} \, dy = \int_{0}^{\infty} e^{-ar^2} 2\pi r \, dr = \frac{\pi}{a}$$

$$\int_{-\infty}^{\infty} e^{-ax^2} \, dx = \sqrt{\frac{\pi}{a}}$$

Gaussian function is even function: therefore

$$\int_{0}^{\infty} e^{-ax^2} \, dx = \sqrt{\frac{\pi}{4a}}$$

Moments: with integration by parts and partial derivatives

$$\int_{0}^{\infty} xe^{-ax^2} \, dx = \int_{0}^{\infty} e^{-t} \frac{dt}{2a} = \frac{1}{2a}$$

$$\int_{0}^{\infty} x^2 e^{-ax^2} \, dx = \frac{\partial}{\partial(-a)} \int_{0}^{\infty} e^{-ax^2} \, dx = -\frac{\partial}{\partial a} \sqrt{\frac{\pi}{4a}}$$

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Continuous variables

Example. Consider the *gaussian* distribution, $\rho(x) = Ae^{-\lambda(x-a)^2}$ where A, a, λ are positive real constatns. (Problem 1.3 of Griffiths QM)

Normalization.

$$1 = \int_{-\infty}^{\infty} \rho(x)\,dx = A\int_{-\infty}^{\infty} e^{-\lambda x^2}\,dx = A\sqrt{\frac{\pi}{\lambda}}, \quad A = \sqrt{\frac{\lambda}{\pi}}$$

Expectation values and standard deviation.

$$\langle x \rangle = \int_{-\infty}^{\infty} x\rho(x)\,dx = \sqrt{\frac{\lambda}{\pi}}\int_{-\infty}^{\infty} xe^{-\lambda(x-a)^2}\,dx = a$$

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2\rho(x)\,dx = \sqrt{\frac{\lambda}{\pi}}\int_{-\infty}^{\infty} x^2 e^{-\lambda(x-a)^2}\,dx = a^2 + \sqrt{\frac{\lambda}{\pi}}\frac{\partial}{\partial(-\lambda)}\int_{-\infty}^{\infty} e^{-\lambda x^2}\,dx = a^2 + \sqrt{\frac{\lambda}{\pi}}\sqrt{\pi}\cdot\frac{1}{2}\lambda^{-3/2} = a^2 + \frac{1}{2\lambda}$$

$$\sigma = \left(\langle x^2 \rangle - \langle x \rangle^2\right)^{1/2} = \frac{1}{2\lambda}$$

Schrödinger Equation

Imagine a particles of mass m, subject to some specified force $F(x, t)$. Then, with the *Newton's second law*, we can determine the particle's position, velocity, momentum, kinetic energy, or any other dynamical variable of interest.

The force can be expressed as the derivative of a potential energy derivative.

$$\mathbf{F} = m\mathbf{a} = -\nabla V$$

Theoretically, by knowing initial conditions, we can completely determine the motion of this particle.

However, quantum-mechanical approach is quite different. In this case, we are looking for the particle's *wavefunction*, and we get it by solving the *Schrödinger equation*.

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

The Schrödinger equation determines $\Psi(x, t)$ for all future time; it has same position with Newton's law, in quantum mechanics. Therefore it is considered as an *axiom*.

Schrödinger Equation

Schrödinger equation has two forms.

Time-dependent Schrödinger equation

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

Time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi, \quad \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V \implies \hat{H}\psi = E\psi$$

$\hat{H}$ is called *Hamiltonian*, whose physical meaning is total energy of the system.

Schrödinger Equation

We can find a justification for Schrödinger equation, though. Start from the classical wave equation.

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u}{\partial t^2}, \quad u(x,t) = \psi(x)\cos \omega t$$

Then we obtain

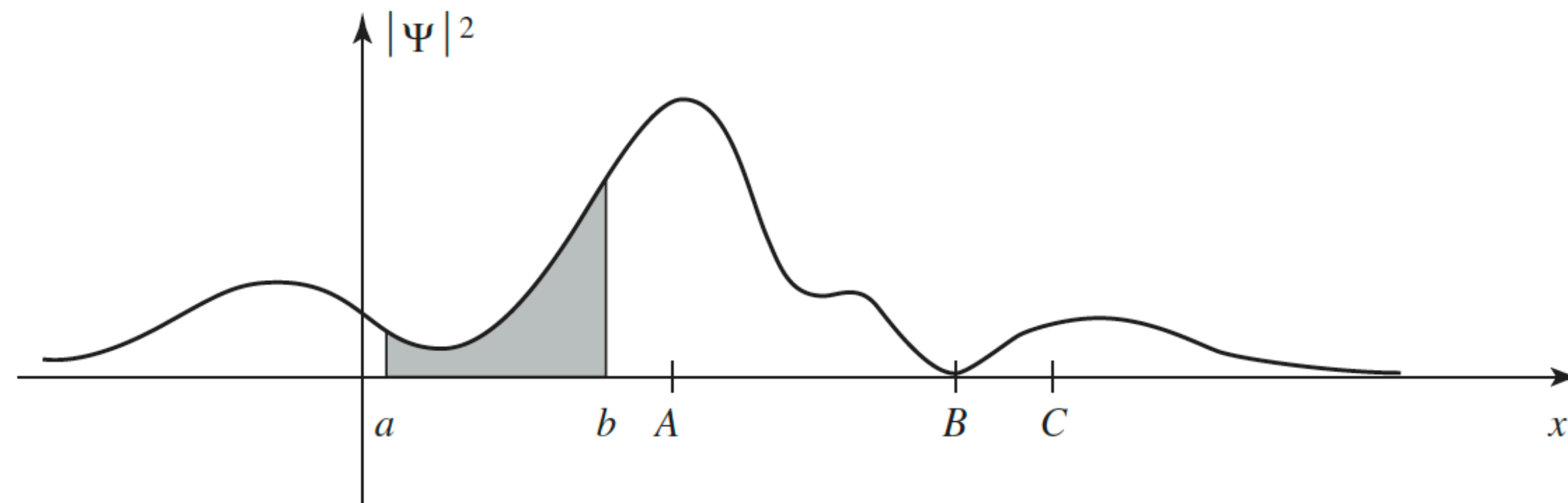$$\frac{d^2\psi}{dx^2} + \frac{\omega^2}{v^2}\psi(x) = \frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi(x) = 0$$

From the de Broglie relation,

$$E = \frac{p^2}{2m} + V(x) \implies p = \sqrt{2m(E - V(x))}, \lambda = \frac{h}{p} = \frac{h}{\sqrt{2m(E - V(x))}}$$

Plug λ into the wave equation: Then we obtain Schrödinger equation.

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V(x)]\psi(x) = 0, \quad -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi(x) = E\psi(x)$$

Wavefunction?

Figure 1.2: A typical wave function. The shaded area represents the probability of finding the particle between a and b. The particle would be relatively likely to be found near A, and unlikely to be found near B.

Wavefunction is spread out in space. How can such an object represent the state of a *particle*?

Born interpretation $|\Psi(x, t)|^2$ gives the probability of finding the particle at point x, time t.

$$\int_a^b |\Psi(x, t)|^2 \, dx = \textbf{probability of finding the particle between } a \textbf{ and } b \textbf{ at time } t$$
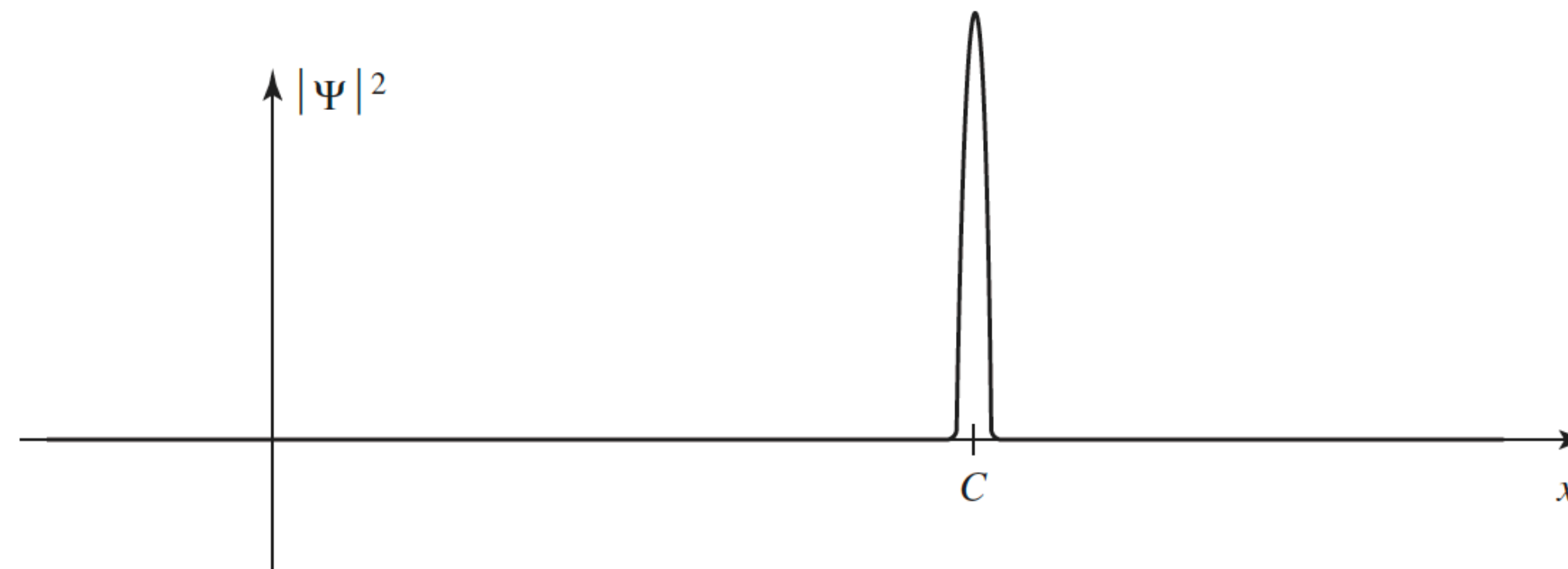
Wavefunction

Therefore, quantum mechanics needs statistical interpretation, which introduces *indeterminacy*.

Question. Where was the particle before our observation?

The widely-accepted interpretation, the *Copenhagen interpretation*, says that *the particle was not really anywhere*.

Right after the *measurement*, wavefunction collapses and particle's location is determined, and the resulr of measurement is *random*: one cannot predict it accurately.
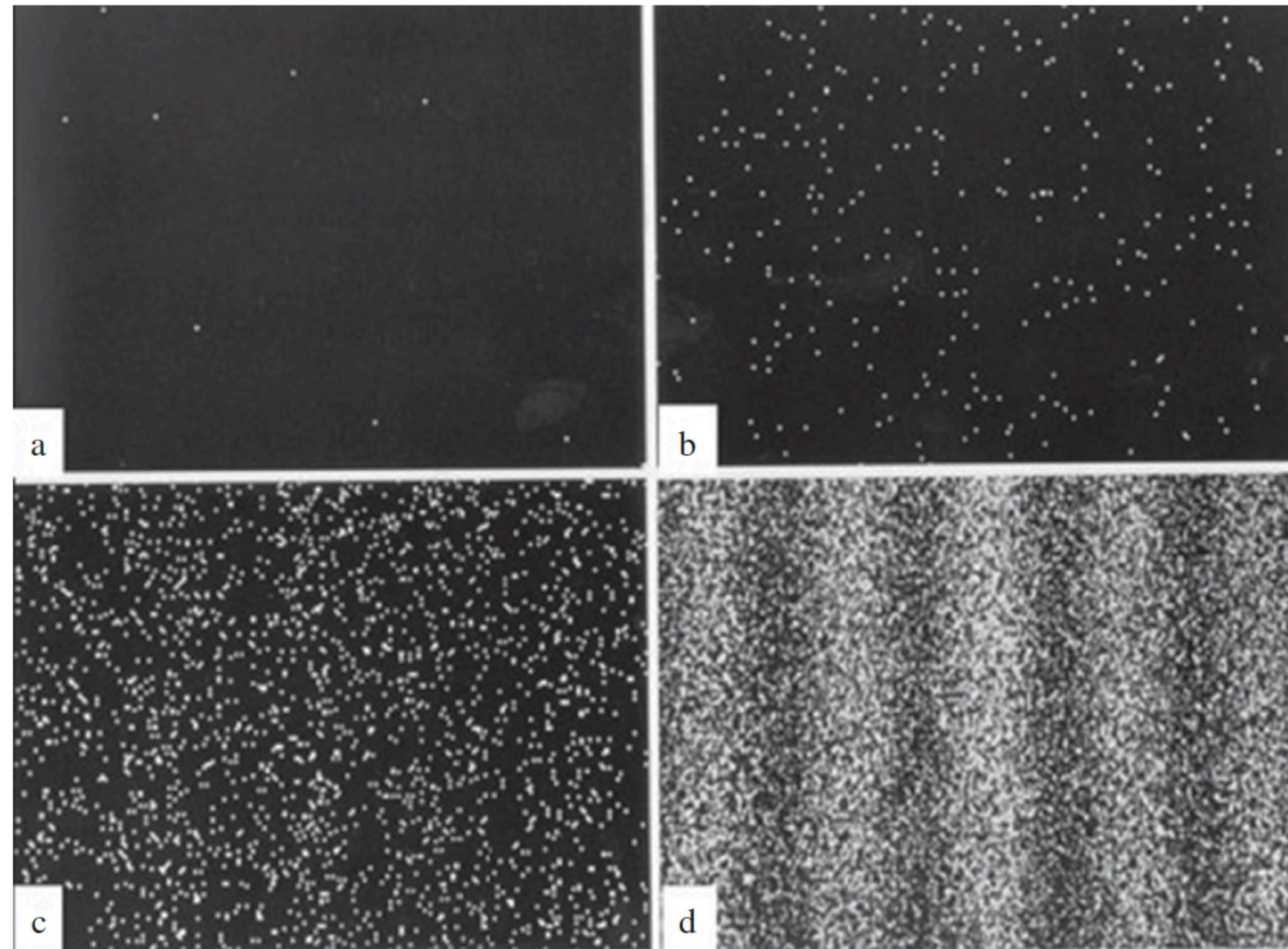

Figure 1.3: Collapse of the wave function: graph of $|\Psi|^2$ immediately *after* a measurement has found the particle at point C.

Electron interference

The wave-like nature of electron

Figure 1.4: Build-up of the electron interference pattern. (a) Eight electrons, (b) 270 electrons, (c) 2000 electrons, (d) 160,000 electrons. Reprinted courtesy of the Central Research Laboratory, Hitachi, Ltd., Japan.

Normalization

From the Born interpretation, we knew that $|\Psi|^2$ has a physical meaning of probability distribution function. Therefore, it should be normalized to unity over all space.

This condition is called *normalization*.

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

Note that physically acceptable wavefunctions should be *square-integrable*. Non-normalizable solutions of Schrödinger equation are therefore rejected.

There are some more criteria that wavefunction should satisfy.

– must not be infinite, over a finite region.
– must be single-valued.
– must be continuous.
– must have a continuous first derivative.

The last criterion is related to *probability current*, which is not our main interest in this class.

Postulates of QM

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Postulate 1. For a system of particles moving under a potential $V(\mathbf{r})$, there is an associated wavefunction Ψ that determines everything that can be known about the system. The time development of this wavefunction is determined by the time-dependent Schrödinger equation:

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

Where $\hat{H}$ is a Hamiltonian *operator*. $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$

Note. Ψ is a complex-numbered function in general.

Note. We usually solve time-independent Schrödinger equation at first. Then we can find time-dependent solution, with appropriate initial conditions. From the $\Psi(x, t)$, we can calculate all properties about the system.