The Schrödinger equation

Erwin Schrödinger found a wave equation for handling de Broglie's matter waves with $\lambda = h/p$, and a potential energy "landscape" U. What went into it?

- Assume that plane waves travel as $\psi(x,t) = \psi_0 e^{-i(\vec{k}\cdot\vec{x} - \omega t)}$.
- Implies that the wave function must satisfy $\dfrac{\partial^2\psi}{\partial x^2} = -k^2\psi$.
- From $k \equiv 2\pi/\lambda$, and $\lambda = h/p$, we find $k^2 = (p/\hbar)^2$.
- From $E_k = p^2/(2m)$ and total energy $E = E_k + U$, we find $k^2 = \dfrac{2m}{\hbar^2}(E-U)$.
- Can be rearranged to give a time-independent equation of

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + U\psi = E\psi \qquad (1)$$

A "particle" must satisfy this wave equation if it is to behave as de Broglie waves do, and if it is to conserve energy and momentum.

Erwin Schrödinger (1887–1961; Nobel Prize 1933)

But what's waving?

- We have a wave equation. What's waving? We will consider the hydrogen atom a few lectures for now. Suffice it to say that what we get are the orbitals you have probably already seen glimpses of.
- But that means the electron is really smeared out? Not consistent with small classical radius or other electromagnetic phenomena.
- So does the wave equation describe the particle, or something about the particle?

Heisenberg and Schrödinger

- Heisenberg, writing to Wolfgang Pauli in 1926:

  > The more I think about the physical portion of Schrödinger's theory, the more repulsive I find it. . . What Schrödinger writes about the visualizability of his theory 'is probably not quite right'; in other words, it's crap.

- Schrödinger's perspective:

  > I knew of [Heisenberg's] theory, of course, but I felt discouraged, not to say repelled, by the methods of transcendental algebra [matrix algebra], which appeared difficult to me, and by the lack of visualizability.

- Yet in May 1926 Schrödinger publishes a paper showing the equivalence of his wave mechanics with Heisenberg's operator theory. Schrödinger visits Heisenberg at Bohr's Institute in October 1926; vigorous discussions. . .

Well. . . Try it anyway

- Before we figure out what's waving, let's just try it out.
- Free particle; 1D; no potential energy; ignore time dependance:

$$E = \frac{p^2}{2m} = \left(\frac{h}{\lambda}\right)^2 \frac{1}{2m} = \left(\frac{h}{2\pi}\right)^2 \frac{k^2}{2m} = \frac{\hbar^2}{2m} k^2$$

(or $k = \sqrt{2mE}/\hbar$) giving (Krane Eqs. 5.12-5.16):

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi = \frac{\hbar^2}{2m}k^2\psi \qquad \text{or} \qquad \frac{d^2\psi}{dx^2} = -k^2\psi$$

- Try $\psi = Ae^{-ikx}$:

$$\frac{d}{dx}\left(\frac{d}{dx}Ae^{-ikx}\right) = A\frac{d}{dx}\left(-ike^{-ikx}\right) = (-ik)^2 A\frac{d}{dx}e^{-ikx} = -Ak^2e^{-ikx}$$

so it works with $A = 1$! But of course it does; we (well, Schrödinger) built it that way. . .

Particle in a box

- Let $U(x) = 0$ for $0 \leq x \leq L$ and $U \to \infty$ elsewhere.
- Recall the time-independent Schrödinger equation of Eq. 5:

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + U\psi = E\psi$$

  In looking at this, we would have to have $E \to \infty$ if there were a nonzero value of ψ in the regions where $U \to \infty$. Therefore we *demand* that we have $\psi = 0$ outside of box.

- Wave should be continuous, so it must be zero at the boundaries $x = 0$ and $x = L$. A sine function does this at $x = 0$, and also at $x = L$ if we require $kL = n\pi$. We therefore guess that the solution is $\psi = A \sin\left(\frac{n\pi x}{L}\right)$ (Serway Eq. 6.18).
- Inside the box with $U = 0$ we have a regular old sine wave satisfying

$$-\frac{\hbar^2}{2m}\frac{d}{dx}\left(\frac{d}{dx}A\sin(\frac{n\pi x}{L})\right) = -\frac{\hbar^2}{2m}\frac{d}{dx}\frac{n\pi}{L}\cos(\frac{n\pi x}{L}) = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 A\sin(\frac{n\pi x}{L})$$

Particle in a box: the conclusion

- Again, we assumed $\psi = A\sin(n\pi x/L)$ inside the box $(0 \leq x \leq L)$ and $\psi = 0$ outside the box.
- We found
$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 A\sin(\frac{n\pi x}{L})$$
- Putting this in the Schrödinger equation of Eq. 5 of
$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + U\psi = E\psi \qquad \text{gives} \qquad \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 A\sin(\frac{n\pi x}{L}) + 0\psi = E\,A\sin(\frac{n\pi x}{L})$$
  so it works as long as $E = (\hbar\pi n/L)^2/(2m)$.
- Not only does it satisfy the Schrödinger equation, but it tells us something important: we have discrete energy states! Let's rewrite what we arrived at for E as $E_n = \frac{\hbar^2\pi^2}{2mL^2}n^2$ (Serway Eq. 6.17).

So. . . What's waving?

- So we can solve for ψ in a simple example (and we'll soon do less simple examples).
- We can get the energies of quantum states.
- But what's waving? And how do we figure out the value of A in $\psi = A\sin(\frac{n\pi x}{L})$?
- Again, think of what Heisenberg wrote to Wolfgang Pauli in 1926:

  > The more I think about the physical portion of Schrödinger's theory, the more repulsive I find it. . . What Schrödinger writes about the visualizability of his theory 'is probably not quite right'; in other words, it's crap.

The Born/Copenhagen interpretation

- See Serway Sec. 6.1. The most commonly accepted interpretation arose from the work of Max Born, and also discussions in Niels Bohr's institute in Copenhagen.
- Matter waves ψ describe not the particle, but its probability amplitude.
- $\psi^\dagger \psi = |\psi|^2$ represents the probability. Therefore we realize that $\int |\psi|^2$ should be normalized to 1.
- Return now to our solution of $\psi = A\sin(\frac{n\pi x}{L})$ for the infinite-walled square well of length L. We require

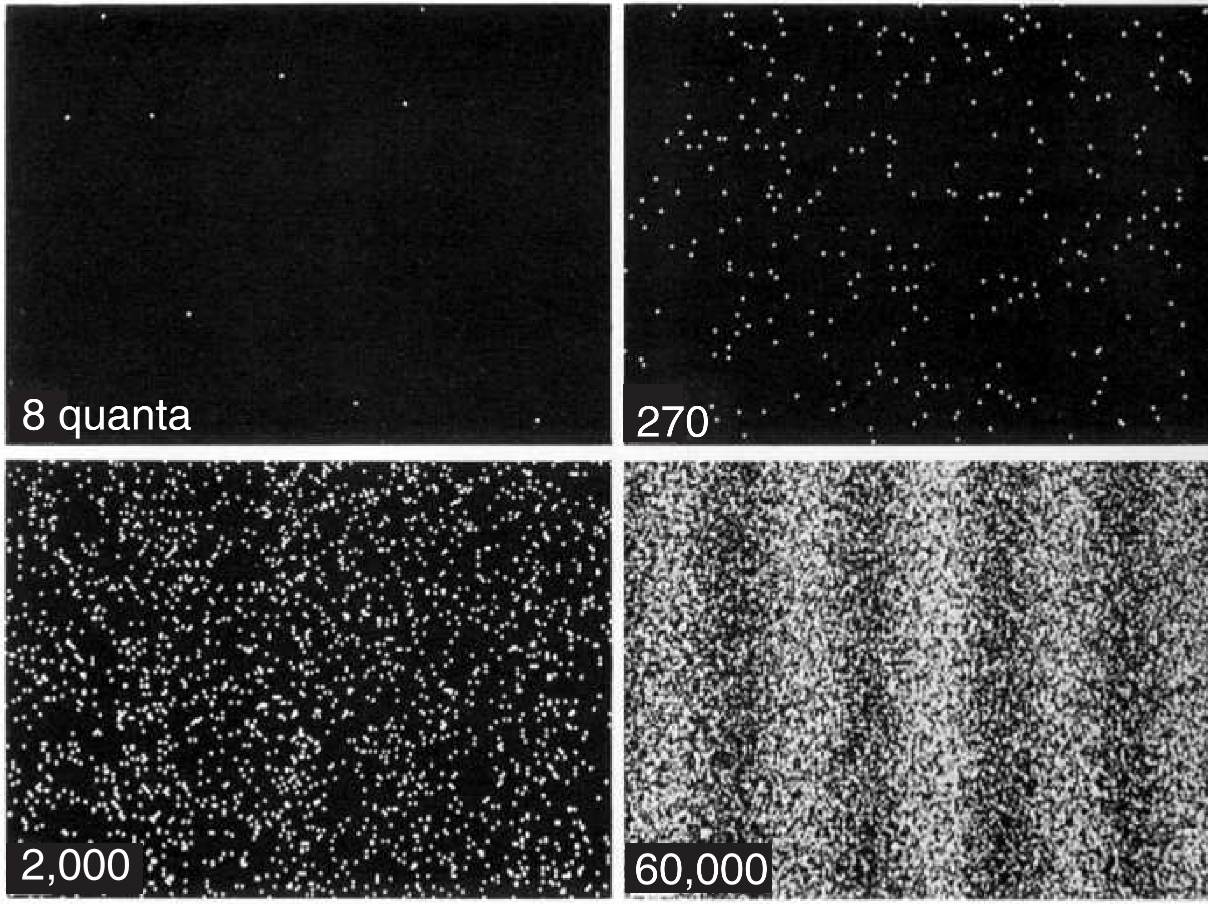
$$\int_0^L |A\sin(\frac{n\pi x}{L})|^2\,dx = A^2 \int_0^L \sin^2(\frac{n\pi x}{L})\,dx = 1$$

The integral can be done in Maple:

```
int((sin(n*pi*x/L)^2),x=0..L);
```

which gives $L/2$ so $A = \sqrt{2/L}$ (see Serway Eq. 6.19). So we now have a properly normalized wavefunction!

Return to electron waves



From A. Tonomura, *Electron Holography* (Springer-Verlag, 1993), p. 14.

Collapsing wavefunctions

- See Serway Sec. 6.1. The most commonly accepted interpretation arose from the work of Max Born, and also discussions in Niels Bohr's institute in Copenhagen.
- The wavefunction ψ represents a probability amplitude (which can have positive or negative values, which can undergo interference, etc.). The probability of a particle being in a particular location is given by $|\psi|^2$. When you determine where a particle is, you change what follows afterwards.
- It's the same difference as in optics, where we use a complex number $Ee^{i\theta} = E(\cos\theta + i\sin\theta)$ to represent the optical field. The real part Re$[Ee^{i\theta}] = E\cos\theta$ represents the electric field E, and the square $\psi^\dagger\psi = (Ee^{-i\theta})Ee^{i\theta} = E^2$ represents the intensity.
- We have a great analogy with quantum mechanics:

Optics		Quantum mechanics
Wavefield $E(x,y)e^{i\theta(x,y)}$	$\leftrightarrow$	Probability amplitude $\psi(x,y)$
Intensity $E^2(x,y)$	$\leftrightarrow$	Probability $|\psi(x,y)|^2$

Light and matter

Property	**Light**	**Matter**
Amplitude A in $\psi = Ae^{-i(kx-\omega t)}$	Electric field E	Probability amplitude
Amplitude squared A^2 in $\|\psi\|^2 = \psi^\dagger \psi$	Electric field squared gives irradiance distribution (from the Poynting vector in classical E&M): $I = \sqrt{\epsilon/\mu}\,(\langle E \rangle)^2$.	Probability amplitude squared A^2 gives probability distrubtion.
Particle arrival	Individual photons arrive at particular locations, but with a probability given by the wave theory calculation of the irradiance $I \propto \|\psi\|^2$.	Individual matter particles arrive at particular locations, but with a probability given by the wave theory calculation of the probability $\|\psi\|^2$.

Schrödinger's cat

Erwin Schrödinger, "The present situation in quantum mechanics," *Naturwissenschaften* **23**, 807–812, 823–828, 844–849 (1935).

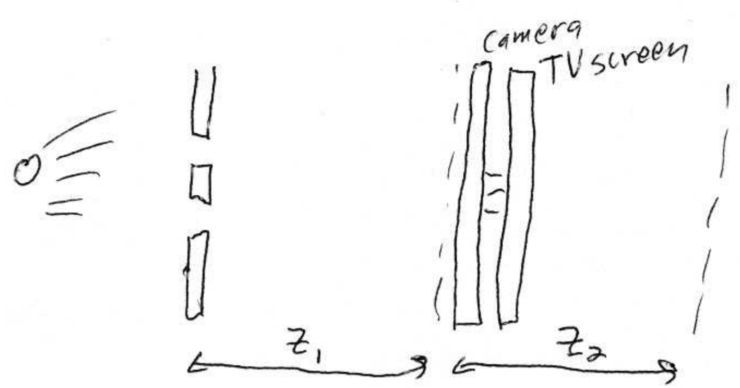
> One can even set up quite ridiculous cases. A cat is penned up in a steel chamber, along with the following device (which must be secured against direct interference by the cat): in a Geiger counter there is a tiny bit of radioactive substance, so small, that perhaps in the course of the hour one of the atoms decays, but also, with equal probability, perhaps none; if it happens, the counter tube discharges and through a relay releases a hammer which shatters a small flask of hydrocyanic acid. If one has left this entire system to itself for an hour, one would say that the cat still lives if meanwhile no atom has decayed. The ψ-function of the entire system would express this by having in it the living and dead cat (pardon the expression) mixed or smeared out in equal parts.

Collapsing wavefunctions with slits

Let's do two experiments (I did these on a computer). They each involve two slits of 5 μm width separated by 5 μm, illuminated by a coherent wave with $\lambda = 500$ nm. We'll consider two downstream planes; the first one is at $z_1 = 0.4$ mm away from the slits, and the second plane is at $z_2 = 0.8$ mm downstream. These distances are not in the far field, so the pattern is a bit different than what you're used to seeing for Fraunhofer diffraction (we use Fresnel diffraction to calculate the pattern).

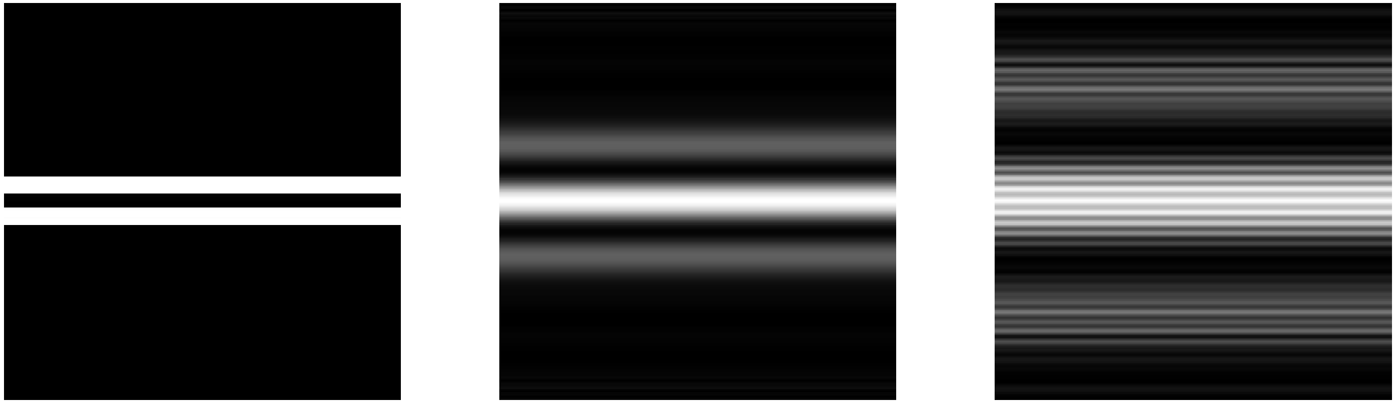
- In **Experiment 1**, we put a camera at plane z_1, and record the intensity pattern. We then remove the camera, and place it at z_2 and record an intensity pattern.
- In **Experiment 2**, we put a TV camera at plane z_1. Whenever it detects a photon at a position, a TV screen emits a dot of light immediately behind at the same position.

Will we see anything different between these two experiments?

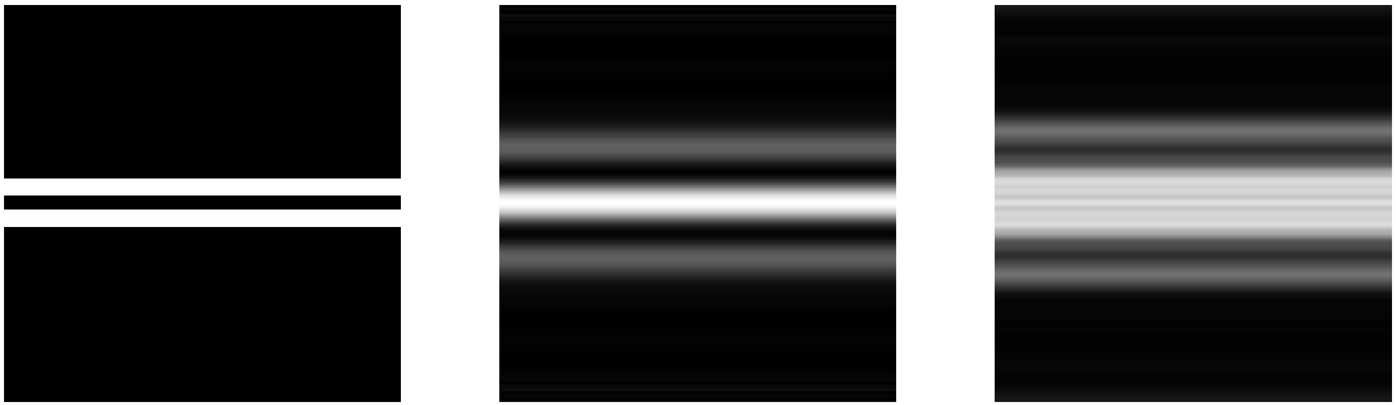


Collapsing wavefunctions with slits II

- Here's **experiment 1** (no TV) at slits, z_1, and z_2:



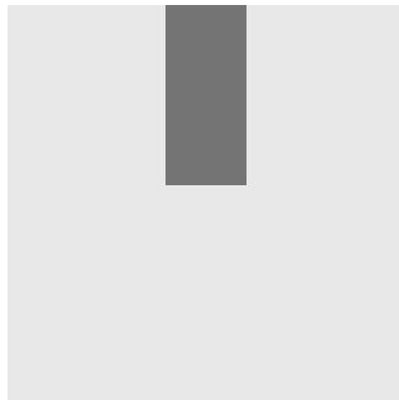
- Here's **experiment 2** (TV) at slits, z_1, and z_2:

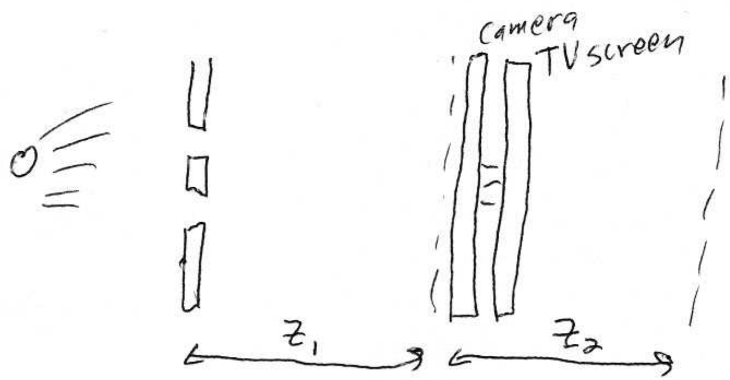


- The result at the downstream plane is *different* because we went from $Ee^{i\theta}$ to $\sqrt{E^2}e^{i\cdot 0}$ at the middle plane; we went from ψ to $\sqrt{|\psi|^2}$!!!

Collapsing wavefunctions with slits III

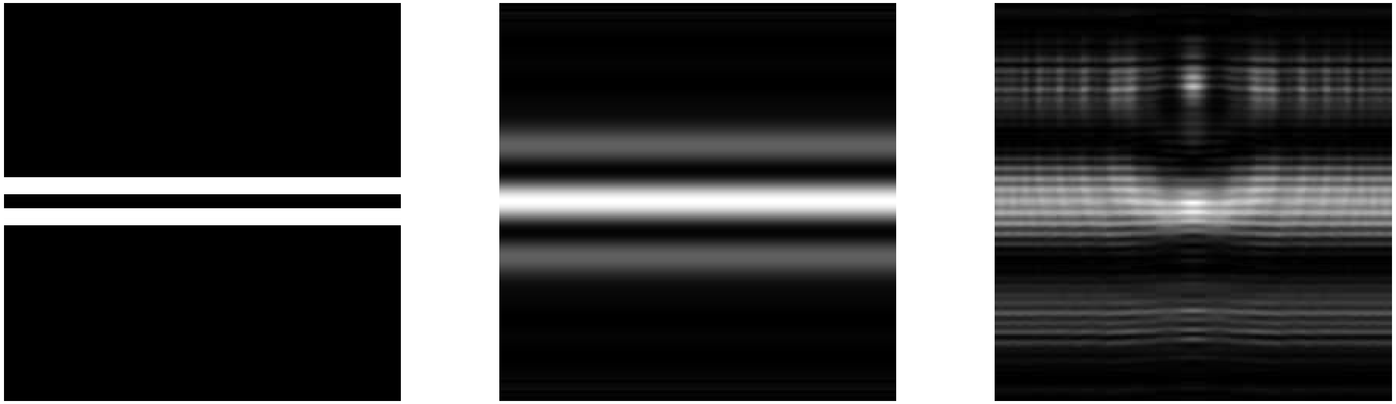
- Now let's repeat the experiment but put a piece of glass (shown here in grey) in just after the middle plane z_1, so that it shifts the phase in the grey area by $\pi/2$:



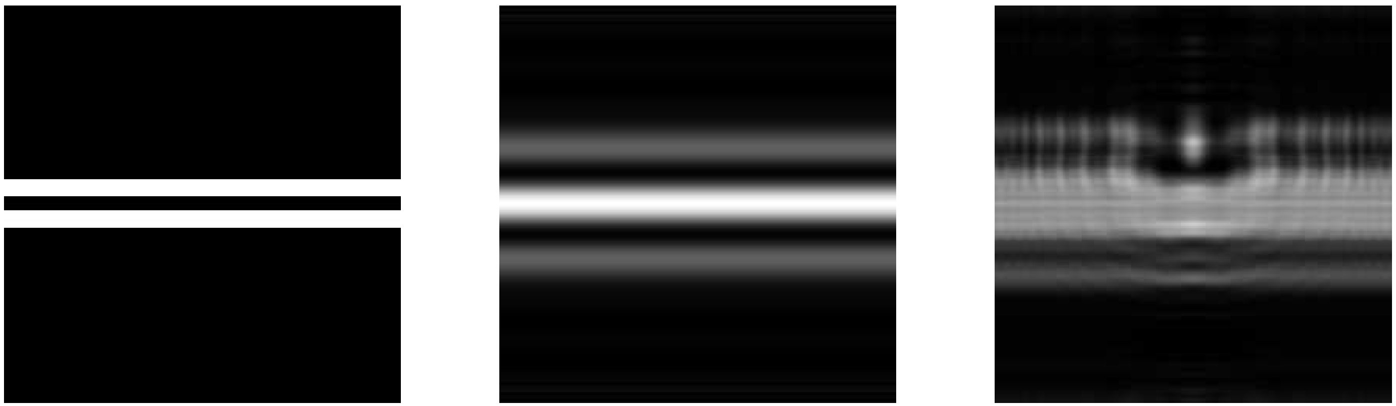


Collapsing wavefunctions with slits IV

- Here's **experiment 1** with the glass after the middle plane:



- Here's **experiment 2** with the glass after the middle plane:

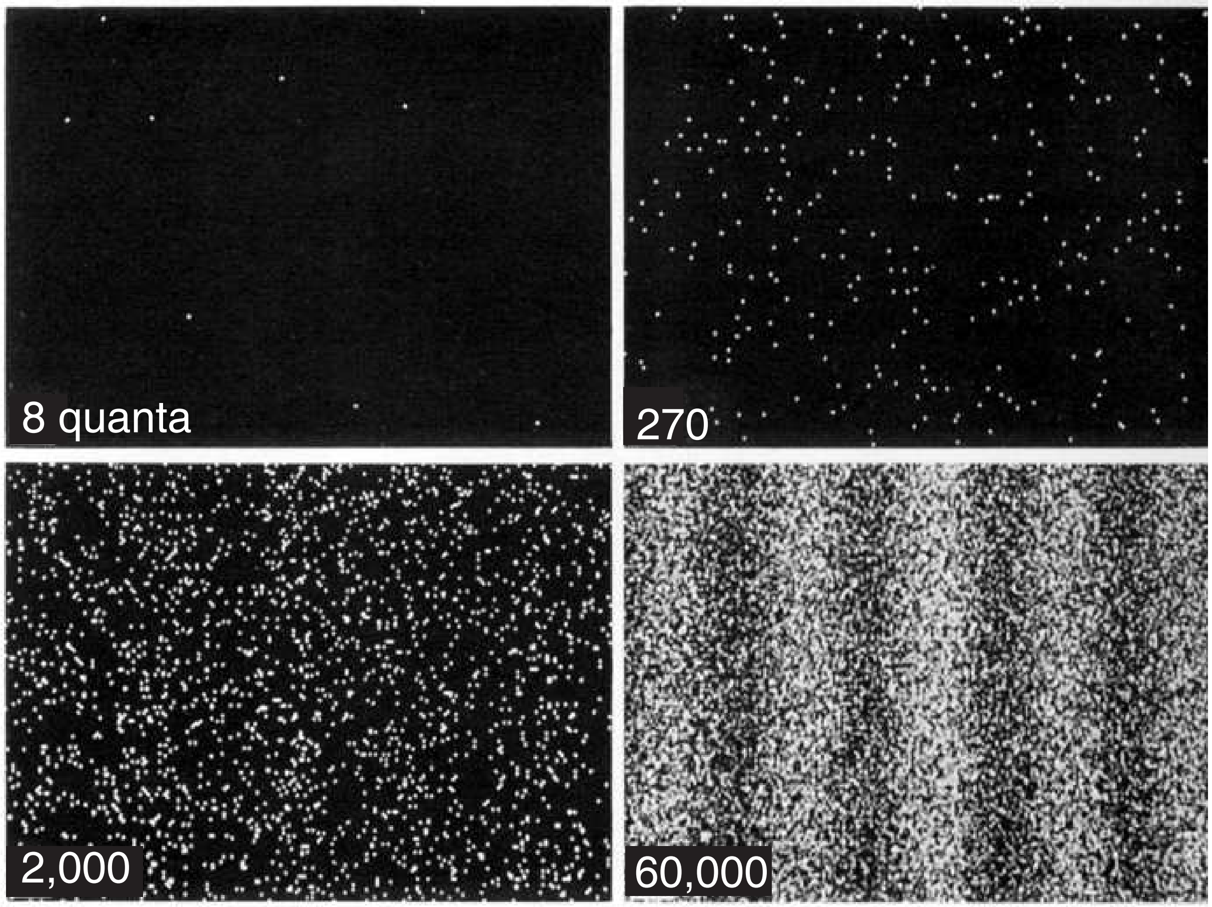


- Again, going from ψ to $\sqrt{|\psi|^2}$ makes a measureable difference!

Collapsing wavefunctions: summary

- So what have we learned? When we make a measurement of where a particle is, we "collapse" the wavefunction from a probability amplitude which can undergo interference, to a probability intensity which cannot.
- The particle's wave function goes through both slits of a double-slit. The particle explores all paths on its journey from A to B. One measurement will just give one example of the choice, with examples weighted according to their probability.
- There is a measurable difference between this picture of probability amplitudes, and tracking particles through the whole chain.
- It's weird, right? Well, get over it! This is how nature works.

Return to electron waves



From A. Tonomura, *Electron Holography* (Springer-Verlag, 1993), p. 14.

The Schrödinger perscription

- Find the potential U. Think of boundary conditions.
- Try a guess of the wave function ψ, by taking its second derivative and seeing if it satisfies

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)+U\psi=E\psi.$$

- This will often give you the energies of the solutions.
- Enforcing $\int\psi^\dagger\psi=1$ will give you the normalization.
- Then ψ gives you the probability amplitude, and $|\psi^\dagger\psi|$ gives you the probability.

Back to the infinite 1D box

- We found

$$\psi = A\sin\left(\frac{n\pi x}{L}\right) \qquad \text{and} \qquad E_n = \frac{\hbar^2\pi^2}{2mL^2}\,n^2$$

for the infinite-walled square well of length L.

- Normalization demands

$$\int_0^L |A\sin(\frac{n\pi x}{L})|^2\,dx = A^2\int_0^L \sin^2(\frac{n\pi x}{L})\,dx = 1$$

The integral can be done in Maple:

```
int((sin(n*pi*x/L)^2),x=0..L);
```

which gives $L/2$ so $A = \sqrt{2/L}$ (see Serway Eq. 6.19).

Infinite box solutions

- Fig. 5.5 of K. Krane, *Modern Physics* (Wiley, 2^{nd} edition, 1995). (similar to Serway Fig. 6.9).
- Notice that the probability distribution is “lumpy”!
- This is not what you would expect from a classical solution, where the particle would have the same probability for all solutions as it bounced back and forth inside the box.

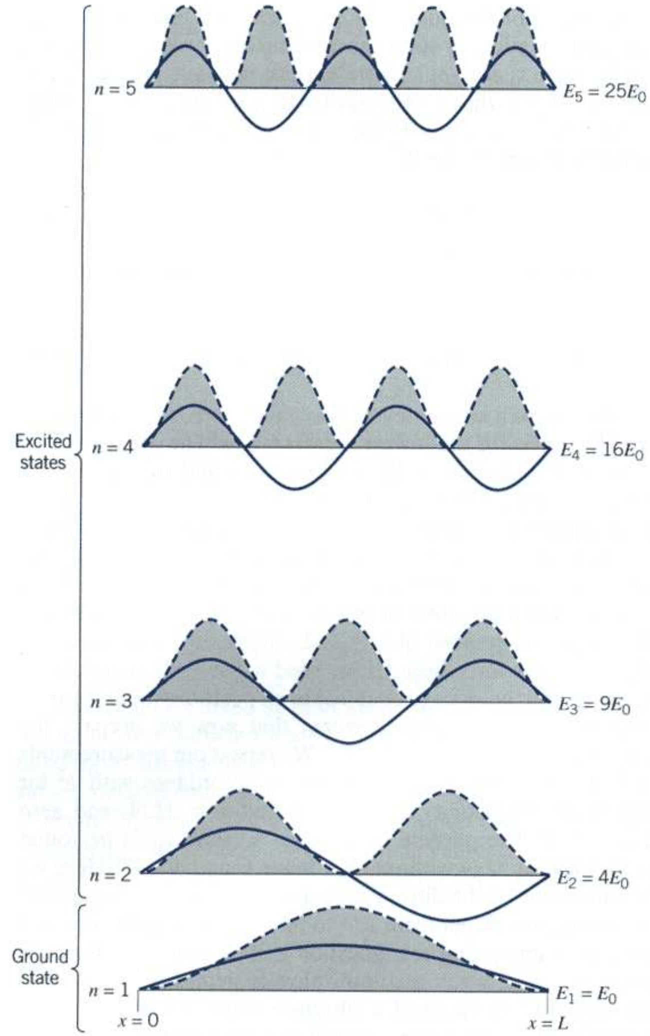


FIGURE 5.5 The permitted energy levels of a particle in a one-dimensional infinite well. The wave function for each level is shown by the solid curve, and the shaded region gives the probability density for each level.

Infinite box in 2D

Square box of dimension L on each side. Assume solution is separable: $\psi(x, y) = f(x)g(y)$.

Trial wavefunction is (Krane Eq. 5.32):

$$\psi(x, y) = A' \sin(\frac{n_x \pi x}{L}) \sin(\frac{n_y \pi y}{L}) = A'B \qquad \text{with} \qquad B \equiv \sin(\frac{n_x \pi x}{L}) \sin(\frac{n_y \pi y}{L})$$

We will need the derivatives:

$$\frac{\partial^2}{\partial x^2} A' \sin(\frac{n_x \pi x}{L}) \sin(\frac{n_y \pi y}{L}) = -A' \frac{n_x^2 \pi^2}{L^2} \sin(\frac{n_x \pi x}{L}) \sin(\frac{n_y \pi y}{L}) = -A' \frac{\pi^2}{L^2} n_x^2 B$$

$$\frac{\partial^2}{\partial y^2} A' \sin(\frac{n_x \pi x}{L}) \sin(\frac{n_y \pi y}{L}) = -A' \frac{n_y^2 \pi^2}{L^2} \sin(\frac{n_x \pi x}{L}) \sin(\frac{n_y \pi y}{L}) = -A' \frac{\pi^2}{L^2} n_y^2 B$$

Schrödinger equation is then

$$\begin{aligned} -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} \right) + U\psi &= E\psi \\ -\frac{\hbar^2}{2m} \left(-A' \frac{n_x^2 \pi^2}{L^2} B - A' \frac{n_y^2 \pi^2}{L^2} B \right) + 0 &= EA'B \end{aligned}$$

More on box in 2D

- Again, we had $\psi(x,y) = A'B$ with $B \equiv \sin(\frac{n_x \pi x}{L})\sin(\frac{n_y \pi y}{L})$, giving

$$
\begin{aligned}
-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2}\right) + U\psi &= E\psi \\
-\frac{\hbar^2}{2m}\left(-A'\frac{\pi^2}{L^2}n_x^2 B - A'\frac{\pi^2}{L^2}n_y^2 B\right) + 0 &= EA'B \\
\frac{\hbar^2\pi^2}{2mL^2}(n_x^2 + n_y^2) &= E
\end{aligned}
$$

  so Schrödinger is satisfied only when $E = \frac{\hbar^2\pi^2}{2mL^2}(n_x^2 + n_y^2)$.

- Normalization $\int_0^L dy \int_0^L dx\, A' \sin(\frac{n_x \pi x}{L})\sin(\frac{n_y \pi}{L}) = 1$ gives $A' = 2/L$

2D box solutions

Krane Fig. 5.7:

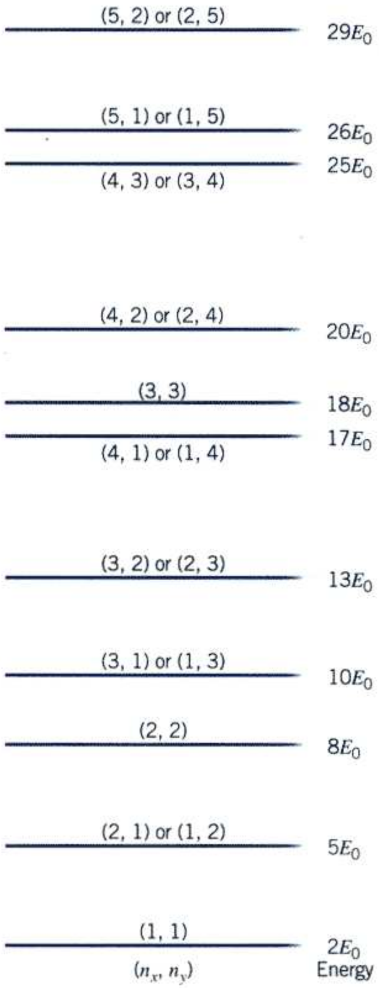


FIGURE 5.7 The lower permitted energy levels of the particle confined to the two-dimensional box.

Krane Fig. 5.8:

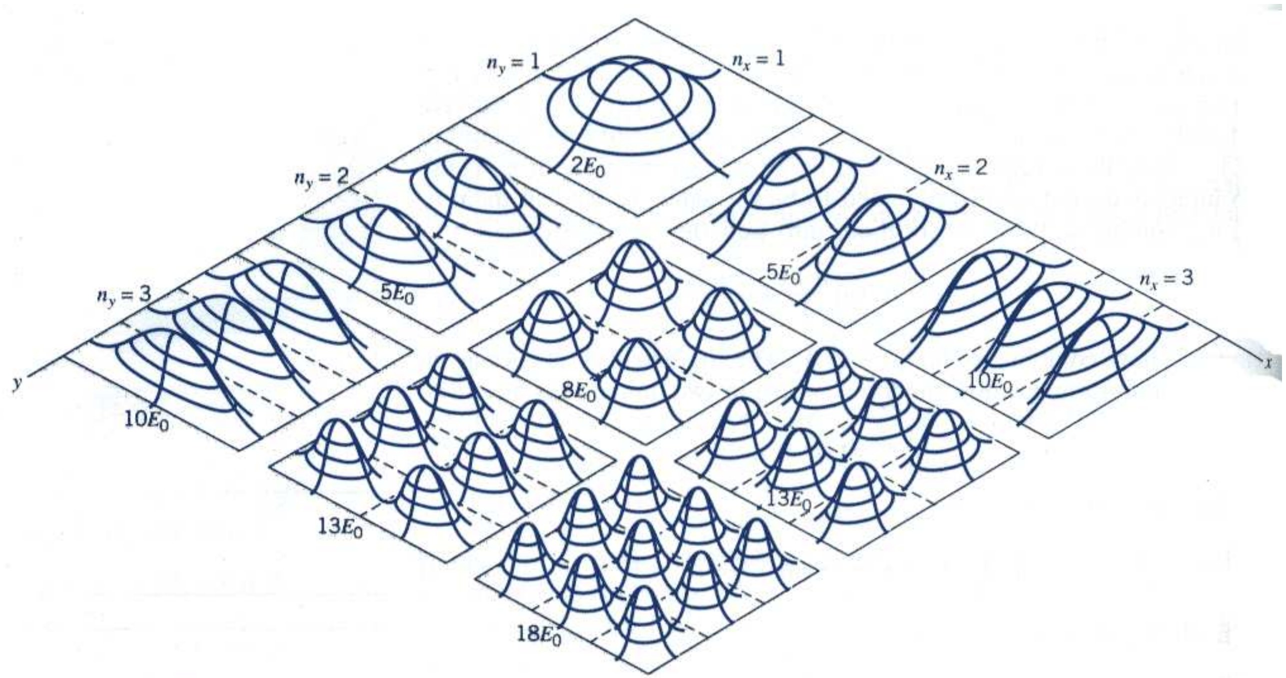


FIGURE 5.8 The probability density ψ^2 for some of the lower energy levels of the particle confined to the two-dimensional box.

Degenerate solutions

Krane Fig. 5.9, where $(7^2 + 1^2) = (5^2 + 5^2)$:

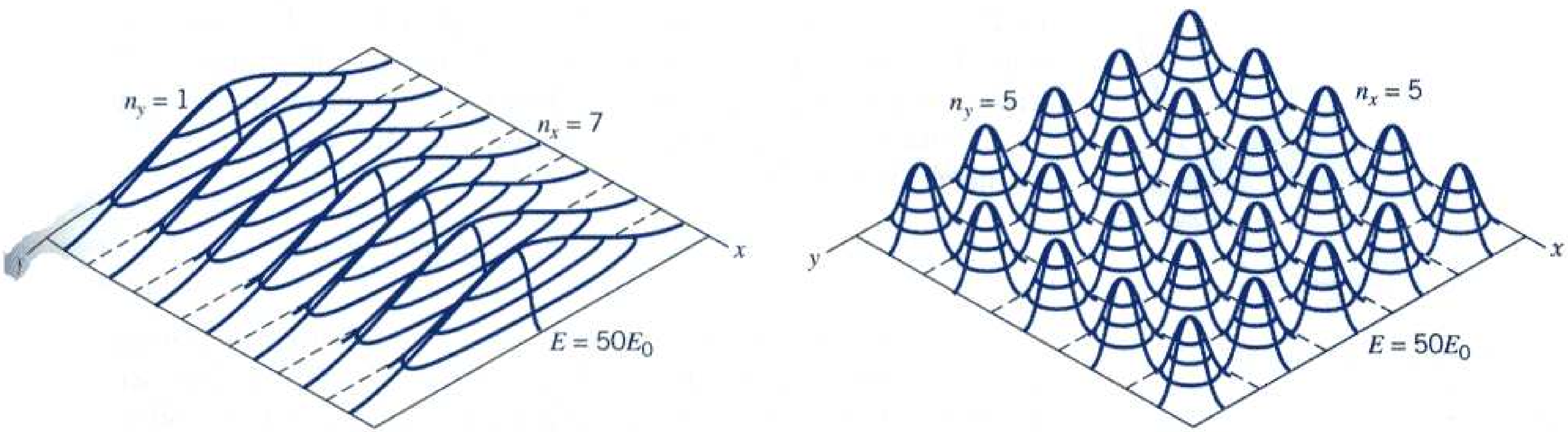


FIGURE 5.9 Two very different probability densities with exactly the same energy.