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

Erwin Schrödinger (1887–1961; Nobel Prize 1933)

The Schrödinger equation

- A wave equation for matter waves that propagate as $\exp[-i(kx - \omega t)]$ with $k \equiv 2\pi/\lambda$ and $\lambda = h/p$.
- Uses $p^2/(2m) = E - U$ (kinetic energy equals total minus potential).
- Full time-dependent form is

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + U\psi = -i\hbar\frac{\partial\psi}{\partial t}. \tag{2}$$

- With a static potential, the time-independent form is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + U\psi = E\psi \tag{3}$$

- Solving for ψ lets you find $E\psi$ or the energy of a quantum state.

Particle in a box

- Let $U(x) = 0$ for $0 \leq x \leq L$ and $U \rightarrow \infty$ elsewhere.
- Looking at Eq. 3, we would have to have $E \rightarrow \infty$ to produce a wave that could satisfy $-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + U\psi = E\psi$. Therefore $\psi = 0$ 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 $\psi = A\sin\left(\frac{n\pi x}{L}\right)$
- Inside the box with $U = 0$ we have

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

Putting this in the Schrödinger equation gives

$$\frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 A\sin(\frac{n\pi x}{L}) = E\,A\sin(\frac{n\pi x}{L})$$

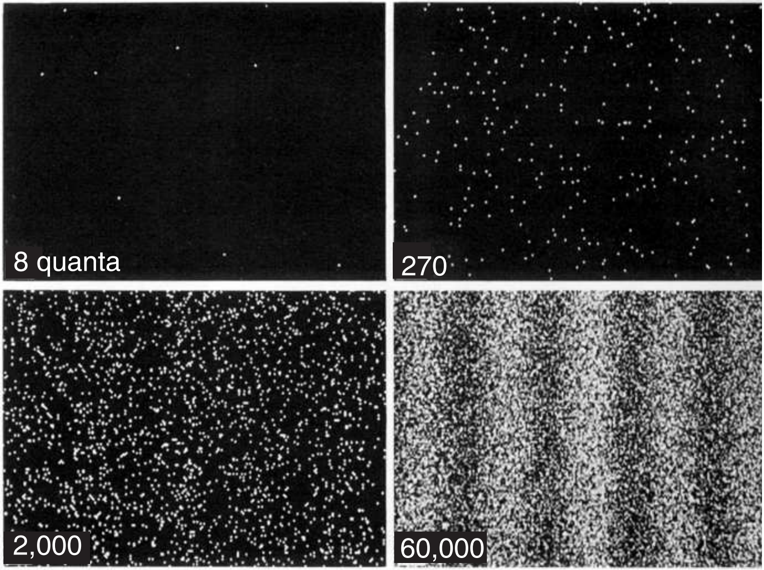
so it works, and we have discrete energy states $E_n = \frac{\hbar^2\pi^2}{2mL^2}n^2$.

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.*

Return to electron waves



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

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: which gives $L/2$ so $A = \sqrt{2/L}$ (see Krane Eq. 5.26).

Max Born (1882–1970; Nobel Prize 1954)

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. 10:

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

  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

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

Particle in a box: the conclusion

- Again, we assumed $\psi = A\sin(n\pi x/L)$ inside the box $(0 \le x \le L)$ 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. 10 of
$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}+U\psi = E\psi \qquad \text{gives} \qquad \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2 A\sin(\frac{n\pi x}{L})+0\psi = E$$
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).