Jan. 7

Schrödinger's Model of Quantum Mechanics

Among the phenomena that require quantum mechanics for their explanation, the first one that I would like to take up is the discreteness of atomic spectra. In the next several lectures, I will present a model of discrete atomic spectra due to Schrödinger. The major success of this model was the explanation, both visualizable and quantitative, of the energy spectrum of the Hydrogen atom. Over the next lectures, I will build up the formalism that we need to give Schrödinger's derivation of the Hydrogen atom energy levels. The discussion will be mostly mathematical. I will not say much about the interpretation of the objects that will arise in our study. Indeed, I will deliberately avoid questions of interpretation as much as possible. Once we are done with the Hydrogen atom, I will go back and discuss these questions in some detail.

Schrödinger's picture is based on a wave model of quantum particles. The study of atoms in the early 1900's led to the intuition that the electron behaved, for many purposes, as a wave. This idea was codified in the 1924 Ph.D. thesis of Louis de Broglie. This thesis presented the idea that electrons should be viewed as waves, with the electron particle somehow residing in the wave. In classical physics, a wave is conveniently written in the form

$$\phi(x,t) = \mathrm{Re}\left[A\, e^{ikx} e^{-i\omega t} \right]$$

Here k is the wavenumber, $k = 2\pi/\lambda$ for wavelength λ, and ω is the frequency, $\omega = 2\pi/T$ for period T. De Broglie identified

$$k \sim p \quad \text{particle momentum} \qquad\qquad \omega \sim E \quad \text{particle energy}$$

Planck had previously introduced the relation between energy and frequency of light

$$E = h\nu \qquad\qquad \nu = 1/T$$

and so de Broglie required the proportionality

$$p = \hbar k \qquad\qquad E = \hbar \omega$$

with

$$\hbar = \frac{h}{2\pi}$$

To extract the momentum and energy from a general waveform, one could act with

$$\vec{p} = -i\hbar \frac{\partial}{\partial \vec{x}} \qquad\qquad E = i\hbar \frac{\partial}{\partial t}$$

This relation is nicely in accord with special relativity. In relativistic notation, it becomes

$$p^{\mu} = i\hbar\, g^{\mu\nu} \frac{\partial}{\partial x^{\nu}}$$

$$p^{\mu} = (E/c, \vec{p})$$

$$x^{\mu} = (ct, \vec{x})$$

$$g^{\mu\nu} = \begin{pmatrix} 1 & & & \\ & -1 & & \\ & & -1 & \\ & & & -1 \end{pmatrix}$$

Schrödinger took this idea and ran with it. He knew that a wave equation, solved in a confined region, would give a discrete spectrum of frequencies. This implied that a wave equation for the electron would potentially lead to a discrete spectrum of energies. To generate an appropriate wave equation, he wrote the Hamiltonian describing a particle

$$E = \frac{p^2}{2m} + V(x)$$

and used the de Broglie transcription to find the equation

$$i\hbar \frac{\partial}{\partial t} = \frac{1}{2m}\left(-\hbar^2 \frac{\partial^2}{\partial \vec{x}^2}\right) + V(x)$$

which should be viewed as acting on a wave function $\psi(\vec{x}, t)$. This gave the *Schrödinger equation*

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{x},t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(x)\right] \psi(\vec{x},t)$$

as a proposal for the wave equation of a quantum electron. The Schrödinger wavefunction $\psi(\vec{x}, t)$ should tell where the electron is located at time t. Presumably, the electron should be near the place where the wavefunction is large. We will make this statement more precise later.

There is something weird about the Schrödinger equation. On the left-hand side, it contains an explicit factor of i. In classical mechanics, the use of complex numbers to describe a wave is a convenience, but here, apparently, it is an essential part of the story. The Schrödinger wavefunction must be complex-valued. We will need to discuss later how to use this wavefunction to derive predictions for experiments, which should be real numbers.

It is not difficult to find a wavelike solution to the Schrödinger equation for a free particle ($V(x) = 0$). Start from the form

$$\psi(x,t) = e^{ikx - i\omega t}$$

Plugging this into the Schrödinger equation, we find the relation

$$\hbar\omega = \frac{\hbar^2 k^2}{2m}$$

or

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

Choosing this $\omega(k)$ for any k gives a solution to the equation. The group velocity of the wave is

$$\frac{\partial \omega}{\partial k} = \frac{\hbar k}{m} = \frac{P}{m}$$

which seems correct.

We can make the Schrödinger equation description of a free particle more intuitive by solving the equation for an initial condition in the form of a *wave packet*, a localized collection of waves. I suggest taking an initial condition

$$\psi(x, t=0) = \int \frac{dk}{2\pi} \, e^{-\frac{\Delta^2}{2}(k-k_0)^2} \, e^{ik(x-x_0)}$$

This is a superposition of waves with wavenumber k within $1/\Delta$ of a fixed value k_0. I claim that this function gives a distribution in real space that is centered at $x = x_0$. To see this, we only need to perform the integral. To do the integral, it is useful, though, not necessary, to know that

$$\int_{-\infty}^{\infty} dy \, e^{-y^2} = \sqrt{\pi}$$

Then, change variables to

$$\bar{k} = k - k_0$$

and rearrange the terms in the exponentials to create an exponential of a perfect square:

$$\psi(x,t=0) = \int \frac{d\bar{k}}{2\pi}\, e^{-\frac{\Delta^2}{2}\bar{k}^2}\, e^{i\bar{k}(x-x_0)}\, e^{ik_0(x-x_0)}$$

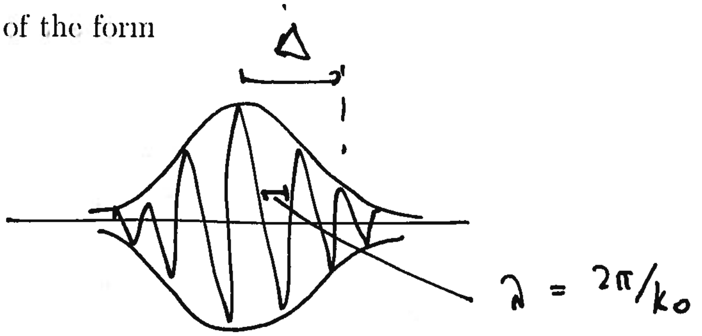
$$= \int \frac{d\bar{k}}{2\pi} \exp\left[-\frac{\Delta^2}{2}\left(\overbrace{\bar{k} - i\cdot 2\frac{(x-x_0)}{\Delta^2}}^{(\bar{k}-ia)^2} - \frac{(x-x_0)^2}{\Delta^4}\right)\right]$$

$$\exp\left[-\frac{\Delta^2}{2}\frac{(x-x_0)^2}{\Delta^4}\right] \exp\left[ik_0(x-x_0)\right]$$

The top line is a constant, proportional to the integral above and thus equal to $1/(2\pi\Delta)^{1/2}$. The functional form of the result is then

$$(\text{const.}) \cdot e^{-\frac{1}{2}\frac{(x-x_0)^2}{\Delta^2}}\, e^{ik_0(x-x_0)}$$

This is a function of the form



It is a bundle of waves with wavelength $\lambda = 2\pi/k$ within a Gaussian envelope of size Δ that localizes the waves to the vicinity of $x = x_0$.

The Schrödinger equation is first order in time, so each initial condition leads to a unique time-dependent solution $\psi(x,t)$. To find that solution, we simply replace the exponential wave in the function above by a solution to the time-dependent Schrödinger equation. Then the unique solution to the Schrödinger equation that evolves from our wavepacket is

$$\psi(x,t) = \int \frac{dk}{2\pi}\, e^{-\frac{\Delta^2(k-k_0)^2}{2}}\, e^{ik(x-x_0)}\, e^{-i\frac{\hbar k^2}{2m}t}$$

To find the physical interpretation of this result, we evaluate the integral. As above, change variables to $\bar{k} = k - k_0$

$$\psi(x,t) = \int \frac{d\bar{k}}{2\pi} \; e^{-\frac{\Delta^2}{2}\bar{k}^2} \; e^{i\bar{k}(x-x_0)} \; e^{ik_0(x-x_0)}$$
$$e^{-i\frac{\hbar\bar{k}^2}{2m}t} \; e^{-i\frac{\hbar\bar{k}k_0}{m}t} \; e^{-i\frac{\hbar k_0^2}{2m}t}$$

and then complete the square in the exponent. This gives $\boldsymbol{\Delta}^2 = \Delta^2 + i\frac{\hbar}{m}t$

$$\psi(x,t) = \int \frac{d\bar{k}}{2\pi} \exp\Big[-\frac{1}{2}\left(\Delta^2 + i\frac{\hbar}{m}t\right)\Big(\bar{k}^2 - \frac{2i}{\boldsymbol{\Delta}^2}\left(x - x_0 - \frac{\hbar k_0}{m}t\right)$$
$$- \frac{1}{\boldsymbol{\Delta}^4}\left(x - x_0 - \frac{\hbar k_0}{m}t\right)^2 \Big]$$
$$\cdot \exp\left[-\frac{1}{2\boldsymbol{\Delta}^2}\left(x - x_0 - \frac{\hbar k_0}{m}t\right)^2\right] e^{ik_0(x-x_0)} \; e^{-i\frac{\hbar k_0^2}{m}t}$$

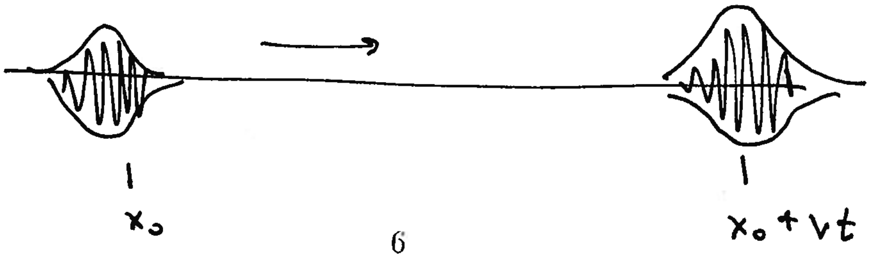
The final result is

$$\psi(x,t) = (\text{const}) \cdot e^{-\frac{1}{2\boldsymbol{\Delta}^2}\left(x - x_0 - \frac{\hbar k_0}{m}t\right)^2} \; e^{ik_0(x-x_0)} \; e^{-i\frac{\hbar k_0^2}{2m}t}$$

The wavepacket then remains localized, though it does spread slowly as a function of time. Its center moves according to

$$x = x_0 + \frac{\hbar k_0}{m}t$$

That is,



The velocity with which the center moves is precisely

$$V = \frac{\hbar k_0}{m} = \frac{p_0}{m}$$

This is Schrödinger's picture of a free quantum particle. The next step is to put the particle in a nonzero potential and see what new phenomena arise. We will do that in the next lecture.