4. The Wave Function.
The Hydrogen Atom.

In the remainder of Part I, we will describe the discovery of the wave function and the peculiarity of its properties.

The light spectrum of the hydrogen atom.

In the late 1800s many physicists thought Newtonian physics was the final theory of the physical world. But as they further explored the properties of matter, several phenomena were found which could not be explained by classical mechanics. The most important was the light spectrum associated with the hydrogen atom. Hydrogen gas was put in a sealed tube and an electric current run thought it. This made the atoms give off light, but its characteristics were not as expected. If one directs the light from the sun through a prism, it is spread out into a *continuous* rainbow of colors. But when the light from the hydrogen gas was sent through the prism, it was found that only certain *discrete* colors (a particular shade of red, a particular shade of green, and so on) were emitted by the gas. It was known that light was a wave and that different colors of light corresponded to different wavelengths. If a grating (very closely ruled lines on glass) was used instead of a prism, the wavelengths of light given off by hydrogen could be measured, with an accuracy better than one part in 10 million. The resulting wavelengths for this discrete spectrum fell into three series (actually there are more, but they are harder to observe) and gave a regular set of results. The observed values for 1 over the wavelength for the different observed lines of the spectrum for the three series are:

$$\begin{gathered} R\left(\frac{1}{4}-\frac{1}{9}\right),\ R\left(\frac{1}{4}-\frac{1}{16}\right),\ R\left(\frac{1}{4}-\frac{1}{25}\right),\ldots \\ R\left(\frac{1}{9}-\frac{1}{16}\right),\ R\left(\frac{1}{9}-\frac{1}{25}\right),\ R\left(\frac{1}{9}-\frac{1}{36}\right),\ldots \\ R\left(\frac{1}{16}-\frac{1}{25}\right),\ R\left(\frac{1}{16}-\frac{1}{36}\right),\ R\left(\frac{1}{16}-\frac{1}{49}\right),\ldots \end{gathered} \qquad (1)$$

where $R=1.097\ 373\ 153\text{x}10^{7}\text{m}^{-1}$ is the Rydberg constant. (Rydberg, a Swedish physicist, found this set of formulas in 1888 by trial and error, not theory.) So the goal of physicists was to find a mathematical theory of the hydrogen atom which predicted these experimentally determined wavelengths. Classical physics was no help because it could not even explain why the atom was stable. It predicts the point electron will spiral into the proton in the center of the H atom so it certainly cannot account for the above spectrum.

The Schrödinger equation for the wave function.

The hydrogen atom spectrum is the kind of problem physicists love. The data to be explained are very accurate and follow a simple rule. But even though the rule is simple, its explanation proved to be extremely difficult to find. It took insights by Planck, Einstein, Bohr, Rutherford, de Broglie and others, over a period of more than 25 years (1900-1926), until finally Schrödinger discovered his famous equation

$$\frac{-\hbar^2}{2m_e}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t} \tag{2}$$

where $\hbar$ is Planck's constant over 2π, *V* is the electrical potential energy, and m_e is the mass of the electron. But the symbol of real interest is the **wave function** ψ. (It's not necessary to understand this calculus equation; its detailed form is given just for fun—and also because it's the equation that, along with gravity, governs our everyday physical world.)

Visualizing the wave function.

In spite of the fact that it worked—it correctly predicted all the observed wavelengths to one part in 10 million—this equation came with problems of its own. In classical physics, the mathematical equations refer only to the positions of the (reputedly existing) *particles*. But there is no reference at all to particles in Schrödinger's equation. There is only the wave function ψ. Thus in 1926, when Schrödinger proposed this equation, physicists had no idea what the wave function represented (and that lack of understanding persists to this day).

However, even though we don't know at this point what ψ symbolizes, we need a way to visualize it, so we can more easily think about it. ψ can be thought of (in simple cases) as a mist, more dense and opaque in some places, less dense and opaque in others. Over most of space, ψ is zero, implying no mist, so that most of "space" is totally transparent. As an example, in the wave function for 'an electron' in a hydrogen atom, ψ is non-zero only in a region measuring about one ten billionth of a meter across, the approximate size of a hydrogen atom.

The Schrödinger equation tells how the shape and density of the wave function change with time. It is a calculus equation, so it has many possible solutions. Every wave function ψ that can *physically* occur corresponds to a *solution of that equation*. Certain kinds of solutions, those with definite energies, are most important. We have roughly drawn the three hydrogen atom states with the lowest energies in Fig. (4-1).

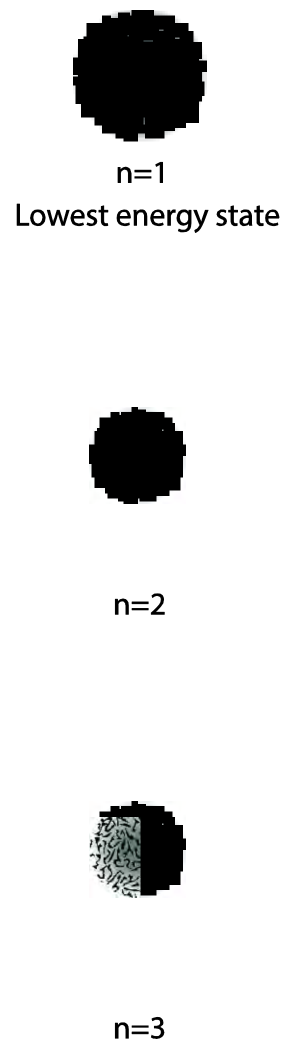

Fig. 4-1

Figure 4-1 Sketches of the wave function for the first three states of hydrogen.

From the states of the electron to the light spectrum of hydrogen.

What is the relation between these three states of the electron wave function and the wavelengths of the spectral lines in Eq. (1)? Suppose we take the 1/4-1/9 ($=1/2^2-1/3^2$) term in the first line of the list above. The mental picture is that

[1] The electron-like wave function is originally in the n=3 state; that is, it has the shape of the third possible state of the electron wave function. This state has energy proportional to $-1/3^2$.

[2] The electron-like wave function then changes to the shape of the n=2 state, with an energy proportional to $-1/2^2$, which is algebraically *less* than the energy of the third state.

[3] To conserve energy in the transition between the two states, the electron-like wave function emits light having energy exactly equal to the difference in the energies of the second and third states. Light of this energy has a definite wavelength, which turns out to agree exactly with the 1/4-1/9 term in the Rydberg formulas. In the Schrödinger theory, the Rydberg constant R is explicitly given in terms of the electron mass and charge, Planck's constant, and a constant from electromagnetic theory, and its derived value agrees with experiment.
[4] By starting from and ending in different states (shapes) for the electron-like wave function, Schrödinger's equation correctly predicts all the experimentally observed wavelengths, so the problem of deriving the hydrogen atom spectrum has been solved.

The essence of the hydrogen atom problem.

The above somewhat detailed explanation of the hydrogen atom spectrum obscures the essence of the approach. The point is that the quantum mechanical mathematics for the wave function alone—with no introduction of the idea of particles—gives results that agree unbelievably well with the very accurately measured wavelengths. Schrödinger's theory gives us a prime example of Wigner's "unreasonable effectiveness of mathematics;" we get agreement with every one of the dozens of observed wavelengths to better than one part in 10 million! Why should mathematics describe physical reality so well? We simply don't know; all we can say is that **matter obeys mathematical laws**.

Note that there is a huge conceptual shift here. There is no reference in the mathematics to an actual point electron; the (conjectured) classical electron, circling the nucleus in some orbit, has been replaced in the quantum mechanics mathematics by the **wave function**. Thus, since all that exists **in the mathematics** is the wave function, there is no evidence—in this problem at least—for the existence of a particulate electron (that is, an infinitesimally small sphere of matter which exists separately from the wave function).

Generalization of the Schrödinger equation.

The success of the Schrödinger equation approach of quantum mechanics is not limited to the hydrogen atom. The suitably modified equation—still with no mention of particles—can correctly predict all those phenomena mentioned at the beginning of Ch. 1. So the Schrödinger equation for the wave function, with its extremely wide range of successful applications, is almost certainly a "correct" theory of the physical universe.

The importance of the hydrogen atom.

The hydrogen atom is the pivot point in our understanding of the physical universe. Before Schrödinger's explanation, we imagined that matter was made up of very small primordial pieces, which is only a relatively small conceptual leap from our everyday perceptions of the physical environment. But after Schrödinger, the universe suddenly became more abstract; it is now—at least in Schrödinger's treatment of the hydrogen atom—made up of wave functions, which we really don't understand. (And which we will understand even less when we see that the wave function can contain several simultaneously existing versions of reality!)

I would add that Schrödinger's discovery of his equation is, to me, the most brilliant and insightful discovery that has ever been made in physical science. (The only other competitors are Maxwell's merging of the theory of light with the theory of electric and magnetic fields, and Einstein's special and general theories of relativity.) How he could have gone from a particle picture of matter to the idea of a wave function obeying a calculus equation is beyond my imagination.

Evaluation:

No controversy here, except perhaps for my opinion on the importance of the Schrödinger equation.