

Lecture 26

- spherically-symmetric solutions of Schrödinger
- Feynman, chapter 16, 19

Spherically-symmetric potentials

To solve the hydrogen atom, we must generalize the Schrödinger equation to three dimensions. This generalization is unique if we require that the equation behave properly under rotation of the coordinate system. One just replaces

$$\frac{\partial^2}{\partial x^2} \rightarrow \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \equiv \nabla^2$$

This is called the Laplacian. the Schrödinger equation in three dimensions is thus

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

So now we understand how to derive the probability amplitudes for continuous systems. One can (and does) then devote an entire course to explaining how to do this in many situations. Hopefully all of you will take such a course. But since we're out of time, I just want to mention one application here. This is the hydrogen atom. Since the nucleus (a proton) is so much heavier than the electron, the proton is not moved much by its interaction with the electron. Thus we can treat it as stationary, and go to the frame where the proton is at rest. Then we study the electron alone, as moving around in a potential

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

Feynman defines a different e which absorbs the $1/(4\pi\epsilon_0)$.

If the problem has spherical symmetry like the hydrogen atom, the analysis simplifies by putting the problem into polar coordinates (r, θ, ϕ) . The Laplacian in spherical coordinates is

$$\nabla^2 f(r, \phi, \theta) = \frac{1}{r} \frac{\partial^2}{\partial r^2} (rf) + \frac{1}{r^2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 f}{\partial \phi^2} \right)$$

Note that just because the potential is spherically symmetric doesn't mean that the solution is spherically symmetric: it can still have an angular dependence. Physically, an angular dependence means that the solution has orbital angular momentum.

The simplest case though is when the particle has no orbital angular momentum, so that the solution is indeed spherically symmetric, independent of angle. These states are called *s* states. The Laplacian simplifies to just the first term. This means that the Schrödinger equation for the stationary *s* states of hydrogen atom simplifies to

$$\frac{1}{r} \frac{\partial^2}{\partial r^2} (r\psi(r)) = -\frac{2m}{\hbar^2} \left(E + \frac{e^2}{4\pi\epsilon_0 r} \right) \psi(r)$$

On the homework you'll check the solutions of this for the amplitudes with the three lowest energies. In general, Feynman shows that the states without angular momentum have energy

$$E_n = \frac{E_1}{n^2}$$

where

$$E_1 = - \left(\frac{1}{4\pi\epsilon_0} \right)^2 \frac{2\pi^2 m_e e^4}{h^2} = -13.6 eV$$

You can look in Feynman to see what happens when you allow the amplitude to depend on the angles θ and ϕ . These correspond to states with orbital angular momentum. You can then derive the conditions we stated earlier. For the n energy level, you find that states with orbital angular momentum $\vec{L} \cdot \vec{L} = l(l+1)\hbar^2$ are allowed with $l = 0, 1, 2 \dots l-1$. Moreover, each level can be filled with up to two electrons: one with $S_z = \hbar/2$ and one with $S_z = -\hbar/2$. Of course what you call the z axis is arbitrary, but we learned in studying two-state systems, that no matter which basis you use, there are the same number of basis states.

For historical reasons, states with $l = 0, 1, 2, 3, \dots$ are labeled *s, p, d, f, \dots*. Thus in the first energy level ($n = 1$) only the *s* states are allowed. Thus in total there are two electrons possible, which are labeled $1s^1$ and $1s^2$. In the second, the *s* and *p* are allowed, so there at most eight electrons allowed (up to $2s^2$ and $2p^6$). In the third, *s, p* and *d* are allowed, and so on. Non-zero angular momentum and interactions among the electrons change the energies: it turns out in multi-electron atoms that $3d$ states are higher energy than $4s$ states, so the $4s$ states fill before the $3d$ ones. This is why the middle portion of the periodic table doesn't start until the fourth row.