

Physics 228, Lecture 14
Thursday, March 10, 2005
Hydrogen Atom; Spin. Ch. 40:5, 41:1,3
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As we discussed last week, there were several early models of atomic structure, of which only the Rutherford model retains even qualitatively relevant features today. The Rutherford model pictured the electrons in large orbits about a very small nucleus in which all the positive charge resides. There are some problems with this classical model, however, in particular that the electrons ought to radiate electromagnetic waves, losing energy and spiralling into the nucleus. We saw how Bohr added some rather ad-hoc rules to the classical picture. Bohr suggested that the electrons follow orbits obeying the laws of classical mechanics, including Coulomb's law, but not radiating as Maxwell's equations would imply. In addition, the possible orbits were limited by a quantization condition on the angular momentum, which we later understood as related to standing wave conditions on the de Broglie waves. The classical mechanics is simple only for a single electron around a nucleus, so we worked this out for a hydrogen atom. We could have also considered hydrogen-like ions, a nucleus with charge Ze stripped of all but one of its electrons. For example, a He^+ ion has a nucleus with $Z = 2$ and a single electron. Then the electron experiences a potential energy from Coulomb:

$$U(r) = -k_e \frac{Ze^2}{r}.$$

This multiplies the force by Z , divides the Bohr radii r_n by Z , multiplies the velocity v_n by Z , and the Bohr energy levels by Z^2 . Thus the circular orbits obeying the quantization condition $L = n\hbar$ have energies

$$E_n = -\frac{k_e^2 e^4 m_e}{2\hbar^2} \frac{Z^2}{n^2} = -\frac{k_e e^2}{2a_0} \frac{Z^2}{n^2}.$$

This model gave a quite good explanation of the spectrum of hydrogen and hydrogen-like ions. But there were a number of details it left out, and it was not really a consistent theoretical framework. With the invention of a really quantum mechanical theory, the picture of the atom changed.

1 States of the Hydrogen Atom

To describe the hydrogen model properly we need to solve Schrödinger's equation for the electron in the presence of the Coulomb potential. Of course the electron can move in three dimensions, so the equation is quite a bit more complicated than the particle in the box we considered. We need to solve the partial differential equation

$$-\frac{\hbar^2}{2m} \vec{\nabla} \cdot \vec{\nabla} \psi(\vec{r}) - k_e \frac{Ze^2}{|r|} \psi(\vec{r}) = E\psi(\vec{r}),$$

where the laplacian $\vec{\nabla} \cdot \vec{\nabla}$ in cartesian coordinates is

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}.$$

Because the situation has a rotational symmetry, however, this problem is best handled using spherical coordinates, so the wave function is

$$\psi(r, \theta, \phi).$$

Due to the spherical symmetry of the problem, the stationary states are described by wave functions which are products of a function of radius $R(r)$ and a function of the angles. Some of the states are spherically symmetric, so there is no dependence on θ and ϕ , but only on r . As for the particle in the box, there is a series of such functions indexed by an integer $n = 1, 2, 3, \dots$. This integer is called the **principal quantum number**, and these spherically symmetric states of the atom are known as *s* states.

Not all the states are spherically symmetric, however, because the electron can have a angular momentum around the nucleus. As in the Bohr atom, the angular momentum is quantized, but this quantization is not an ad-hoc assumption but comes out of solving the Schrödinger equation. The orbital angular momentum of the electron is described by the **orbital quantum number** ℓ which determines the magnitude of the angular momentum, and another integer (called the **orbital magnetic quantum number**) m_ℓ . The word magnetic in the name only has to do with how it is measured; m_ℓ actually tells us all we can know quantum mechanically about the direction of the angular momentum. There are restrictions on these quantum numbers. All are integers, and:

$$n \geq 1, \quad 0 \leq \ell \leq n - 1, \quad -\ell \leq m \leq \ell,$$

so for a given value of n (which can be any positive integer), there are n possible values for ℓ : $0, 1, \dots, n-1$, and for each value of n and ℓ , there are $2\ell + 1$ possible values of m_ℓ : $m_\ell = -\ell, -\ell + 1, \dots, 0, \dots, \ell$.

It turns out that for the solution of Schrödinger's equation for the hydrogen atom, the energy of the state with quantum numbers n, ℓ , and m_ℓ only depends on the principal quantum number n and is what Bohr said:

$$E_n = -13.606 \frac{Z^2}{n^2} \text{ eV}. \quad (Z = 1 \text{ for hydrogen}).$$

All the states with a given n are said to form a **shell**. These have peculiar one-capital-letter names beginning with K, but for most purposes the shell is referred to by its n value. All the states with a given n and a given ℓ are called a **subshell**, and they have more peculiar one-lower-case-letter names s, p, d, f, g, h . The letter names of subshells are important to know, because they are used to describe the electronic structure of atoms. Thus the three states with $n = 2, \ell = 1$ are referred to as the $2p$ subshell.

2 Spin

Planets going around the sun revolve around the sun, with an orbital angular momentum $\vec{r} \times \vec{p}$. They also rotate about their own axis, with additional angular momentum. Elementary particles do that too, and the additional angular momentum is called the particle's **spin**.

The *spatial* dependence of the wavefunction is completely described by the three quantum numbers n, ℓ , and m_ℓ , and those describe quantum mechanically the orbit of the electron. But it turns out that the electron has some other motion as well. All evidence points to an electron being a point particle rather than an extended object, but nonetheless it can spin about its own center, somewhat like a baseball or a planet. To specify its state, the wave function must depend not only on its position in space but also on the direction of its spin. Unlike a baseball, however, an electron can only spin at one speed, and in one of two directions, up and down.

S&B 42.5
spinning
electron
 $3'' \times 2 \frac{3}{4}''$

This is a little confusing — it does not mean that two directions are special, and an electron can't spin along the positive x axis. Rather it is like the polarization of a photon, where the photon can be polarized in any direction, but these are not independent states for directions not perpendicular to each

other. For electrons, we pick some direction arbitrarily, and then the electron can have a spin of $\pm\frac{1}{2}\hbar$ in that direction, two possibilities described by the **spin magnetic quantum number** $m_s = \pm\frac{1}{2}$.

The quantum numbers n , ℓ , m_ℓ , and m_s completely specify the state of the electron. While n can be any positive integer, for each value of n there are only a limited number of choices for the other quantum numbers, so only a finite number of states. For example. for $n = 3$, we can have $\ell = 0, 1$, or 2 . If $\ell = 0$, m_ℓ must be zero, and there are only the two states $m_s = \frac{1}{2}, -\frac{1}{2}$. Thus there are two states in the 3s subshell. For $\ell = 1$ we can have $m_\ell = -1, 0$, or 1 , and each of these can be combined with either of the two values for m_s , so there are 6 states in the 3p subshell. Finally for $\ell = 2$, we can have $m_\ell = -2, -1, 0, 1$, or 2 , and each of these five choices can be combined with either of the two choices of spin, to give 10 states in the 3d subshell. In all, the $n = 3$ shell thus has 18 states. As we shall see, this counting explains the periodic table of the elements, so this simple counting has profound effects.

Full state of electron specified by n, ℓ, m_ℓ, m_s

Shell	sub-shell	n	ℓ	m_ℓ	m_s	number of states
K	1s	1	0	0	$\frac{1}{2}, -\frac{1}{2}$	2
L	2s	2	0	0	$\frac{1}{2}, -\frac{1}{2}$	2
L	2p	2	1	-1, 0, 1	$\frac{1}{2}, -\frac{1}{2}$	6
M	3s	3	0	0	$\frac{1}{2}, -\frac{1}{2}$	2
M	3p	3	1	-1, 0, 1	$\frac{1}{2}, -\frac{1}{2}$	6
M	3d	3	2	-2, -1, 0, 1, 2	$\frac{1}{2}, -\frac{1}{2}$	10

3 Hydrogen Wave Functions

The general problem of working out the wave function $\psi(r, \theta, \phi, m_s)$ is a problem in partial differential equations, and while it can be done elegantly, it is beyond the scope of this course. Still, it would be a good idea to have some picture of what these wave functions look like, because the behavior of atoms can be described in terms of these functions which tell us where the electron is likely to be found.

The $\ell = 0$, or s states, are the easiest, because their wavefunctions have no dependence on the angles, so the wave function is spherically symmetric. Easiest of all is the $n = 1$ state,

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0},$$

where a_0 is still the Bohr radius. The dependence on r is a simple decreasing exponential. The square of the wave function gives the probability of finding the electron, per unit volume. So the probability that the electron is found within an infinitesimal volume dV at distance r from the nucleus is

$$|\psi_{1s}|^2 dV = \frac{1}{\pi a_0^3} e^{-2r/a_0} dV,$$

and the most likely spot for the electron is on top of the nucleus. But that is misleading; it is better to ask what the probability is for the electron to be within dr of being a distance r from the nucleus. That is, what is the probability $P(r)dr$ that the electron is in a spherical shell of radius r and thickness dr centered on the nucleus? The volume of the shell is its area times its thickness, $dV = 4\pi r^2 dr$, so

$$P(r)dr = |\psi|^2 \times 4\pi r^2 dr$$

and

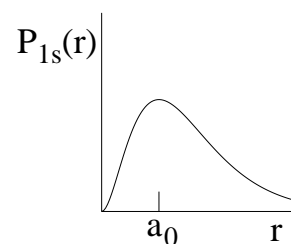
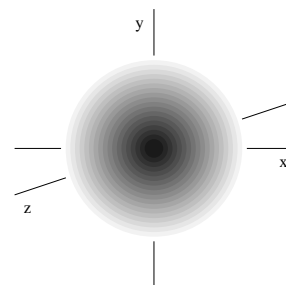
$$P(r) = 4\pi r^2 |\psi|^2.$$

For our 1s state this gives

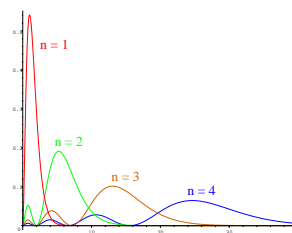
$$P(r) = \frac{4r^2}{a_0^3} e^{-2r/a_0}.$$

From the plot, or by differentiating to find the maximum, we find that the most probably value of r is a_0 , not zero.

Notice that the Bohr picture, with the electron is at a definite radius, is not correct.



The higher n states have the same sort of exponential dependence on r , but with a larger range, $\psi(r) \approx e^{-r/na_0}$, and also have extra polynomials in r multiplying them. This produces zeros in the wave function at certain values of r . For example, the 2s state has a factor $(2 - r/a_0)$ which produces a zero probability of being exactly at twice the Bohr radius, and a good probability that the electron is at about $5a_0$. Higher n values have more zeros and are dominantly at larger values of r , though all have some chance of being close to the nucleus.



$P(r)$ for s waves

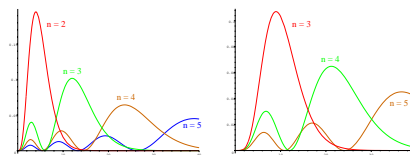
The states which have $\ell > 0$ are not spherically symmetric. For example, a p state with $m_\ell = 0$ has a wave function which is $zR(r)$, which vanishes in the $x-y$ plane. For the $n = 2$ shell R is a decaying exponential and the wave function looks like S&B Fig. 42.9(c). There are two other p states, which can be expressed as $xR(r)$ and $yR(r)$, or alternatively as $m_\ell = \pm 1$, which are combinations of the $xR(r)$ and $yR(r)$ states. $m_\ell = +1$ is much like a plane wave polarized at 45° , a combination of plane waves polarized in the y and z directions.

S&B 42.9
 p -wave
 functionals
 $7'' \times 2 \frac{3}{4}''$

For $\ell > 0$, where the wavefunctions are not spherically symmetric, it is difficult to present the picture of the probability density in three dimensions. If we look at a slice of the electron cloud with $x = 0$ we can plot the probability of the electron being at a point near that plane. That is what this program does. Lets try it for $n = 4, \ell = 2, m_\ell = 1$.

Do wave-
 function
 demo

For a given ℓ the lowest possible principle quantum number is $n = \ell + 1$. For that shell the radial function $R(r)$ has no zeroes except at $r = 0$. The higher n states have extra factors which push most of the wave function further from the nucleus.



p wave $P(r)$ d wave $P(r)$

We will focus more attention on ℓ and m next time, and discuss how this leads to the atoms we know from the periodic table.

4 Summary

- The states of a hydrogen atom are solutions of Schrödinger's equation with a potential $U(r) = -k_e \frac{e^2}{r}$.
- The solutions are indexed by
 - **principle quantum number** $n = 1, 2, 3, \dots$
 - **orbital quantum number** $\ell = 0, 1, \dots, n - 1$
 - **orbital magnetic quantum number** $m_\ell = -\ell, -\ell + 1, \dots, \ell - 1, \ell$

but the full state of the electron also needs to have the **spin magnetic quantum number** specified as $\pm \frac{1}{2}$.

- All states with a given n are called a **shell**, and all of those having a given ℓ are called a **subshell**, and are given letters s, p, d, f,
- The energy of the state depends only on the principle quantum number

$$E_n = -\frac{13.606 \text{ eV}}{n^2}.$$

- The hydrogen wave functions have a decaying exponential e^{-r/na_0} , possibly multiplied by polynomials in r (for $n > \ell + 1$) and by polynomials in (x, y, z) of order ℓ . The probability to lie within a range of values of r is proportional to $r^2|\psi|^2$ and peaks at some nonzero value, a_0 for the ground state 1s.