Hydrogen Atom Structure and Spectra

Our next application of quantum mechanics is to the simplest of all atoms: hydrogen. The spectra of atoms (and molecules) play an immensely important role in astronomy, because it is only by looking at such spectra that we can figure out the composition of objects, their redshift, how fast they move, and so on. Recently, there has even been a suggestion that at high redshifts the spectra change in a way most easily explained by a varying "fine structure constant", which can be calculated from the quantum mechanical effect it has on electron orbitals. We'll see whether this evidence holds up, and in this class we won't be going into that kind of detail, but spectra are where quantum mechanics meets astronomy most squarely.

First, let's think of an atom purely classically. Imagine that we treat a hydrogen atom as an electron moving in circles around a proton. The electron is therefore accelerated, so it radiates. The total energy at a given instant is the (negative) potential energy plus the kinetic energy, and for a circular orbit the total energy is negative (it's half the potential energy, by the virial theorem). Therefore, loss of energy means that the electron moves closer to the proton, so the acceleration is greater and the energy loss is greater. Classically, this process would run away and within a tiny fraction of a second the atom would collapse.

As a semi-classical try to deal with this, Bohr suggested a quantization rule that the angular momentum of the electron had to be $\hbar$ times a nonzero integer. If we assume this but otherwise keep our classical "solar system" picture, then for the ground state we have $V = -e^2/r$, $K = \frac{1}{2}m_e v^2 = e^2/2r$ (from the virial theorem), and $L = m_e v r = \hbar$. The total energy is $-e^2/2r$, which for this angular momentum is $E = -m_e e^4/2\hbar^2 = -13.6$ eV. This happens to be exactly right, and if you put in $2\hbar$, $3\hbar$, and so on you get the right energy spacing ($E(n\hbar) \propto 1/n^2$).

But why should the angular momentum be quantized? Let's take a different approach: from the uncertainty principle we know that if an electron is confined to a small volume then it has a large momentum. In particular, let's say that $p = \hbar/\Delta x$, or if the electron is within a distance r of the proton then $p = \hbar/r$. Then, independent of quantization effects, we'd like to know the ground state of the atom, which is where the total energy is minimized. The total energy is $p^2/2m_e - e^2/r$, which is $\hbar^2/(2m_e r^2) - e^2/r$. This reaches a minimum at $r = \hbar^2/(m_e e^2)$, so that again we get the exact answer $E = -m_e e^4/2\hbar^2$.

This is too good to be true. In fact, we're just lucky to get the right factors in these cases, although getting the dependences right is *not* an accident. It is, however, helpful to have this general picture before moving on to the equations.

Let's bite the bullet and do it for real! We are looking for stationary states of the atom, i.e., we want to use the time-independent Schrödinger equation. The potential energy

$V(\mathbf{r}) = -e^2/r$, so it is spherically symmetric and therefore it is best to use the Schrödinger equation in spherical coordinates. For now, let us remain somewhat general by treating a spherically symmetric potential, in which $V(\mathbf{r}) = V(r)$. We'll substitute in the Coulomb potential $V(r) = -e^2/r$ later.

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi\ . \tag{1}$$

If we write out the ∇^2 operator in spherical coordinates we get the intimidating expression

$$\nabla^2 = \left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\ . \tag{2}$$

Ulp. The resulting partial differential equation looks nasty. In general, a differential equation need not have an analytic solution, and partial differential equations can be especially tricky. It is often useful to make a guess at the form of the solution to see if it can be simplified. One guess here is that because the potential is independent of θ and ϕ, maybe the eigenfunctions can be written as a product of a radial factor and an angular factor. This is called separation of variables, and we've already done that with the time component by separating out the factor $\exp(-iEt/\hbar)$.

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)\ . \tag{3}$$

Let us write the Schrödinger equation in somewhat more compact form by defining

$$\nabla^2 = \mathcal{R} + \frac{1}{r^2}\mathcal{L}^2 \tag{4}$$

where

$$\begin{aligned} \mathcal{R} &\equiv \left(\tfrac{\partial^2}{\partial r^2} + \tfrac{2}{r}\tfrac{\partial}{\partial r}\right)\ , \\ \mathcal{L}^2 &\equiv \tfrac{1}{\sin\theta}\tfrac{\partial}{\partial\theta}\left(\sin\theta\tfrac{\partial}{\partial\theta}\right) + \tfrac{1}{\sin^2\theta}\tfrac{\partial^2}{\partial\phi^2}\ . \end{aligned} \tag{5}$$

Then the separation of variables produces

$$\left[-\frac{\hbar^2}{2m}\mathcal{R}R(r)\right]Y(\theta,\phi) - \frac{\hbar^2}{2mr^2}[\mathcal{L}^2Y(\theta,\phi)]R(r) + V(r)R(r)Y(\theta,\phi) = E\,R(r)Y(\theta,\phi)\ . \tag{6}$$

Note that $\mathcal{R}$ only affects $R(r)$, whereas $\mathcal{L}^2$ only affects $Y(\theta,\phi)$. If we multiply each term by

$$\frac{2mr^2}{\hbar^2}\frac{1}{R(r)Y(\theta,\phi)}\ , \tag{7}$$

we get

$$\frac{r^2\mathcal{R}R(r)}{R(r)} + \frac{2mr^2}{\hbar^2}[E - V(r)] = -\frac{\mathcal{L}^2Y(\theta,\phi)}{Y(\theta,\phi)}\ . \tag{8}$$

The left hand side is only a function of r, whereas the right hand side is only a function of θ and ϕ. The only way they can be equal is if both are equal to a constant, call it Λ.

Remember, by the way, that $\mathcal{R}$ and $\mathcal{L}^2$ are operators, so they aren't just multiplied by $R(r)$ and $Y(\theta,\phi)$. We therefore have two equations:

$$\begin{aligned} \mathcal{R}R(r) + (2m/\hbar^2)[E - V(r)]R(r) &= (\Lambda/r^2)R(r) \ , \\ \mathcal{L}^2 Y(\theta,\phi) &= -\Lambda Y(\theta,\phi) \ . \end{aligned} \tag{9}$$

Whew! Let's sit back and take stock of what this means. First, we have shown that if the potential is spherically symmetric, then the wavefunction can be broken into a radial part and an angular part. This is intuitively reasonable. Note also that the energy only appears in the radial eigenfunction equation. This suggests the possibility that it is only the radial function that enters into the energy. Finally, note that $\hbar$ never enters explicitly into the angular part of this equation. This suggests that the functions $Y(\theta,\phi)$ are not just quantum mechanical. Indeed, they are called spherical harmonics, and enter any time one has spherical symmetry and modes. For example, when one thinks about oscillation modes of a star (such as the Sun), spherical harmonics are used to describe them even though quantum mechanics has nothing to do with the oscillations.

Let's get a flavor for the wavefunctions by setting $\Lambda = 0$ and looking for solutions to the Coulomb problem $V(r) = -e^2/r$. We notice that Y =constant is a solution of the angle equation, so let's assume that and focus on the radial equation. The radial equation becomes

$$\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) R(r) - \frac{2m}{\hbar^2}\left(-e^2/r - E\right) R(r) = 0 \ . \tag{10}$$

It is still far from obvious how one should solve this equation in a systematic way. In such situations, it is useful to make an educated guess. Note that both the terms in parentheses have one term that has a $1/r$ in it, and one without. If we choose a function whose form doesn't change when the derivatives are taken, we might be able to match up the terms. Therefore, let's try $R(r) \propto \exp(\lambda_1 r)$, realizing that the constant in front will cancel out so that we may as well set it to 1.

$$\begin{aligned} (\lambda_1^2 + 2\lambda_1/r)\exp(\lambda_1 r) - (2m/\hbar^2)(-e^2/r - E)\exp(\lambda_1 r) &= 0 \\ \lambda_1^2 + 2mE/\hbar^2 + 2\lambda_1/r + 2me^2/(\hbar^2 r) &= 0 \ . \end{aligned} \tag{11}$$

In order for this equation to be true at all radii, the constant term must be zero and the term proportional to $1/r$ must be zero, independently. This implies

$$\begin{aligned} \lambda_1 &= -me^2/\hbar^2 \\ E &= -\hbar^2\lambda_1^2/2m = -me^4/(2\hbar^2) \ . \end{aligned} \tag{12}$$

This is the energy of the ground state. For $m = m_e = 9.11 \times 10^{-28}$ g, we get 13.6 eV, the ground state binding energy of hydrogen.

What does this mean? **Ask class:** What is the typical radius beyond which the probability density drops off significantly? In an exponential of the form $\exp(-r/r_0)$, one can say to order of magnitude that $r \sim r_0$ is where the probability drops off, so in this case $r_0 = \hbar^2/(m_e e^2) = 5.2 \times 10^{-9}$ cm, the Bohr radius. We also need to ask whether the wavefunction we have derived satisfies the constraint that the squared modulus can represent a probability. It can indeed, because $\exp(-2me^2r/\hbar^2)$ integrates to a finite value over all space, so it can be normalized and can therefore represent a probability.

Now let's see what we can find about other states. When we picked our trial wavefunction for the ground state, we were able to find a solution because we had two free parameters (λ_1 and E) and needed to solve two equations (both the r^{-1} and r^0 terms had to vanish). **Ask class:** if we keep an exponential factor in front, how can we generalize the form of the wavefunction so that we still have as many unknowns as equations? Note that if instead of a constant in front of the exponential, we have a polynomial of degree n (i.e., the highest power of r is r^n), then we have $n+2$ equations (the r^{-1}, r^0, $r^1, \ldots, r^n$ terms must all vanish). It may appear at first that we have $n+3$ unknowns: $n+1$ from the coefficients of the polynomial, plus E and the factor in the exponential, but remember that the overall normalization of the wavefunction does not enter into the eigenfunction equation (the normalization is determined by the condition that the probability must integrate to 1 over all space). Therefore, there are only $n+2$ free parameters, so we can solve the equation with a polynomial in front of the exponential. Let's try the next case, where we assume $\psi = (a+r)\exp(\lambda_2 r)$, where λ_2 is not necessarily the same as λ_1.

$$\begin{aligned}
[(a+r)\lambda_2^2 + 2\lambda_2 + (2/r)(a+r)\lambda_2 + 2/r]\exp(\lambda_2 r) - (2m/\hbar^2)(-e^2/r - E)(a+r)\exp(\lambda_2 r) &= 0 \\
r(\lambda_2^2 + 2mE/\hbar^2) + (a\lambda_2^2 + 4\lambda_2 + 2me^2/\hbar^2 + 2mEa/\hbar^2) + (1/r)(2a\lambda_2 + 2 + 2mae^2/\hbar^2) &= 0\ .
\end{aligned} \tag{13}$$

This is a little more complicated, but on solving you get

$$\begin{aligned}
\lambda_2 &= -me^2/2\hbar^2 \\
E &= -me^4/(8\hbar^2) \\
a &= -2\hbar^2/me^2\ .
\end{aligned} \tag{14}$$

Ask class: what does this mean, in comparison with the ground state wavefunction? The energy is 1/4 of the ground state energy. We also notice that the wavefunction goes to zero at $r = 2\hbar^2/me^2$. If we were to continue to higher and higher order polynomials, we would notice that for n being the highest power of r, the energy is proportional to $1/(n+1)^2$.

The wavefunctions we have considered thus far have $\Lambda = 0$. This corresponds to zero angular momentum. If we were to look at the angular eigenfunction equation $\mathcal{L}^2 Y(\theta,\phi) = -\Lambda Y(\theta,\phi)$ in detail, we would find that solutions exist only if $\Lambda = \ell(\ell+1)$, where ℓ is a nonnegative integer. Let's try $\ell = 1$ and see what solutions we can find.

In the same spirit as before, we can try a wavefunction of the form $\psi \propto \exp(\lambda r)$, where λ is undetermined. However, we notice that now the right side of the radial eigenfunction equation has $2/r^2$ when the common factor of $\exp(\lambda r)$ is cancelled out, and no $1/r^2$ term exists on the left, so this equation cannot be solved.

We then move up one rank of polynomials, and consider $\psi \propto (a+r)\exp(\lambda r)$. Once again, the term proportional to a gives a term like a/r^2 on the right hand side, but no corresponding $1/r^2$ term on the left. This is only consistent if $a=0$, so we can try instead $\psi = r\exp(\lambda r)$. The radial eigenfunction equation becomes

$$\begin{aligned} (\lambda^2 r + 2\lambda + 2\lambda + 2/r)\exp(\lambda r) + (2mEr/\hbar^2 + 2me^2/\hbar^2)\exp(\lambda r) &= (2/r)\exp(\lambda r) \\ r(\lambda^2 + 2mE/\hbar^2) + (4\lambda + 2me^2/\hbar^2) + 2/r &= 2/r\ . \end{aligned} \tag{15}$$

The $2/r$ terms cancel out, and we are left with

$$\begin{aligned} \lambda &= -me^2/(2\hbar^2) \\ E &= -me^4/(8\hbar^2)\ . \end{aligned} \tag{16}$$

Therefore, although the ground state cannot have any angular momentum, the first excited state can, and the energy is the same as the energy of the first excited state without any angular momentum. There's one thing we should note about the wavefunctions with and without angular momentum. **Ask class:** for zero angular momentum, is the probability density at $r=0$ zero or nonzero? It is nonzero in both cases we've looked at. **Ask class:** how about for nonzero angular momentum? The wavefunction has a factor of r, so the probability density at the origin is zero. This corresponds to classical intuition of orbits: zero angular momentum can pass straight through the center, but nonzero will always run into a "centrifugal barrier" and fail to reach the origin, for a $1/r^2$ force law or $1/r$ potential. Incidentally, the mass m here should really be the reduced mass $\mu = mM/(m+M)$, where M is the mass of the nucleus, but since the proton mass is nearly 2000 times the electron mass, it's a small correction.

It should be emphasized that the techniques we've described here are rather brute force techniques. In principle, inspired guessing can solve eigenfunction equations (if they can be solved at all), but if you pursue quantum mechanics further you'll see that specific problems (such as this one or the harmonic oscillator) can be approached with special techniques that are more elegant.