

Thoughts for the Day
CH301 Fall 2010
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The Hydrogen Atom

All we need to do is solve the Schrödinger equation.

So we need to write down the Hamiltonian that has the kinetic energy part like every other QM problem and the potential energy part which is different in each problem. Here the problem has spherical symmetry so we will choose to write the problem in spherical coordinates.

Here our three dimensions are not the Cartesian x , y , and z . Instead we right position as a function of r the distance from the origin, and two angles θ and ϕ . Theta (θ) is the angle away from the z -axis, and Phi (ϕ) is the angle away from the x -axis in the xy -plane. The easiest way to think about this is on a globe. When $\theta = 0$ you are at the north pole. When $\theta = \pi/2$ (in radians) you are at the equator (this is 90°). When $\theta = \pi$ you are at the south pole. Phi determines where you are in the “east-west” direction. Phi can range from 0 to 2π .

This makes taking derivatives slightly more complicated (which we won't do much of). It also makes taking integrals more complicated, which we will do. This is because when we are integrating we are essentially adding up the function over a certain region of space. In Cartesian coordinates if I integrate in three dimensions the volume for an infinitesimal change in coordinate is the same at all points $dV = dx dy dz$. However, in spherical coordinates the volume depends on both r and θ . This is fairly easy to visualize again with the globe. I ask you to integrate by walking around the globe. If you integrate the variable ϕ from 0 to 2π , this distance is a strong function of both r and θ . For $\theta = 0$ (the north pole). You can essentially turn in place and cover all angle ϕ . At the equator this is a long distance (the circumference of the earth). In addition, this distance depends on r . The circumference at the equator clearly depends on the radius of the earth. We need to take these two affects into account when integrating. The results is that the volume element dV in spherical coordinates is

$$dV = r^2 \sin\theta dr d\theta d\phi$$

That is we have the changes in the coordinates and a factor of $r^2 \sin(\theta)$ in addition.

This will be important when we look at probability densities.

Now on the Schrödinger equation.

What is the Hamiltonian.

In spherical coordinates it is

$$\hat{H} = \frac{-\hbar^2}{2m} \nabla^2 + V(r)$$

where ∇^2 is the 2nd derivative in spherical coordinates

and

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

The potential $V(r)$ is simply Coulomb's law for an electron at a distance r from a nucleus of charge $+Ze$.

Now we just have to find the wavefunctions.

We discover that they can be broken into two parts. One part which is only a function of the radius and another that is only a function of the angles.

Moreover, we have three dimensions so we end up with three quantum numbers.

They are

n the principle quantum number

l the angular momentum quantum number

m the magnetic quantum number

The radial part of the wavefunction depends on n and l , the angular part on l and m .

Most importantly, it turns out the energy only depends on n . What are the energies.

$$E_n = \frac{-Z^2 e^4 m_e}{8\epsilon_0^2 h^2 n^2}$$

$$E_n = \frac{-Z^2}{n^2} \text{ in Rhydbergs}$$

Does this look familiar? It should. It is the same as the energies from the Bohr model. Remember this correctly matched the experimental line spectra for the H-atom. As such, we should hope our new solution also predicts these values. In fact, many would say the QM solution is “exact”. An it is, in the sense that it is the exact solution to the Schrödinger equation. And thus if QM is actually what governs the world and we have written down the correct Hamiltonian, then it is exact. We don’t address the first one. This we’ll simply take for granted. The 2nd one however, we need to address as there are something we have not included. Most importantly, relativity. However, as we have tried to figure out in many HW problems. We would expect relativistic effects for atoms with large nuclear charges. Thus our solutions will be very good for the H atom. And potentially very bad for Au⁺⁷⁸.

What else do we know about the solutions?

The quantum numbers are related.

n can range from 1, 2, 3,....

l has values starting at 0 and going up to n-1

m has values starting at -l and going up to +l

Thus for n=3 all the possibilities are

n = 3	l=2	m=-2,-1,0,1, 2
	l=1	m=-1,0,1
	l=0	m=0

for a total of 9 degenerate (same energy) solution. The total number of function for any value of n is n².

What do these functions looks like? They are simply mathematical functions. They have two parts,

the radial part $R_{n,l}(r)$ and the angular part $Y_{l,m}(\theta,\phi)$

You can see these functions and many plots of them in the book.

Things to think about.

The difference between the radial wavefunction R(r) and the probability density $r^2[R(r)]^2$?

The probability density has a factor of r^2 in it to take into account the volume element getting larger as r increases.

The functions have names that are based on their shape. The shape comes predominately from the angular part and mostly from l . Thus the names depend on l .

$l=0$ is S, $l=1$ is P, $l=2$ is D, $l=3$ is F, $l=4$ is G,

What do the radial functions look like? Mostly they are an exponential decay multiplied by a polynomial. The polynomial gets higher order as n increases. Thus they all decay to zero as r goes to infinity. This is good. The electron should be mostly by the nucleus. They also get more “wiggly” as n increases. This to say the wavefunction changes sign and there are nodes. Just like the particle in a box, the number of nodes increases with energy. In the H-atom the number of nodes is equal to $n-1$.

Let's think about the S functions.

For $n=1$ the radial part here is peaked at $r=0$ and then decays away exponentially. The probability that the electron is at $r=0$ is still however zero as the volume element is equal to zero at this distance. This means the radial distribution function has a peak away from the nucleus and then decays away at large r . For higher n the function is similar but multiplied by a polynomial. The decay is also “slower” and thus the peak of the function is at larger r . In addition, the polynomial causes the wavefunction to change sign. This creates nodes in the probability distribution. Thus with one node ($n=2, l=0$) there are two peaks. However, the second is larger than the first. This means as I move away from the nucleus first the probability increases, then peaks, then goes to zero, then increases again to a larger probability, and then decays away to zero. For the 3s function it is the same but with 2 nodes and three peaks. The largest peak is always the one farthest from the nucleus.

This now brings up the difficult issue of how to plot such a 3-d function. Often what is done is to choose a radius (say the most probable distance) and draw a sphere. However, this means we can't “see” inside to notice that there are nodes. Another scheme is to imagine a slice through the sphere to show the nodes. Or one can simply plot the radial function and know that for $l=0$ the angular function is constant (thus spherical = same at all angles).

What is I want to know “how big is a H-atom”. This is a problem as the probability has a finite value extending out to $r = \text{infinity}$. However, at large r this probability though finite is very very small. Thus I might as at what distance do I have to go out until I have a 95% probability of finding the electron. Or 99%. Or 99.9%...

To do this I would need to solve an integral. What would it be?

I need to integrate up the probability (the wavefunction squared x volume element) until I get a value of 0.95 (for 95%). What would this look like?

$$\int_0^{r_{95}} \int_0^\pi \int_0^{2\pi} R_{n,l}^2(r) Y_{l,m}^2(\theta, \phi) r^2 \sin \theta dr d\theta d\phi$$

This is really three integrals. The first is integrating over r. The second over theta. The third over phi. I can put the radial part together and the angular part together and I get

$$\int_0^{r_{.95}} R_{n,l}^2(r) r^2 dr \int_0^\pi \int_0^{2\pi} Y_{l,m}^2(\theta, \phi) \sin \theta d\theta d\phi = 4\pi \int_0^{r_{.95}} r^2 R_{n,l}^2(r) dr$$

This reduces to simply an integral over r, because all of the angular function when integrated up over all angles are equal to 4π .

Thus what am I looking for? I want to find the limit of the integration $r_{.95}$ such that the integral is equal to 0.95

$$0.95 = 4\pi \int_0^{r_{.95}} r^2 R_{n,l}^2(r) dr$$

If I integrate to $r = \text{infinity}$ then I get 1. How far do I have to integrate to get 0.95? That is the distance I'm looking for.

P-orbitals.

Now we have to think about visualizing both the radial part and the angular part. The radial part is very similar except that the functions start out with a value of zero at $r=0$ (that is both the function and the radial distribution are 0 at $r=0$). Then they peak. Then they decay. As n increases they get nodes.

The angular part we need to try to "visualize" by plotting the value of the function as a function of angle. This is often done by plotting the length of a vector (arrow) away from the origin as a function of angle. For $Y_{1,0}$ we see this is simply $\cos(\theta)$. Thus the maximum is at $\theta = 0$, the function is zero and changes sign at $\pi/2$, and then there is a minimum at $\theta = \pi$. Visualized in 3-d this yields a sort of "dumbbell shape". Thus the dumbbell shape of the p-function.

The p functions have 1 angular node (at $\pi/2$). Thus for $n=2$ there is only 1 node ($n-1$).

For 2s the one node is a radial node.

For 2p the one node is an angular node.

For the p function we run into more difficulty visualizing the functions as $Y_{1,1}$ and $Y_{1,-1}$ turn out to be complex functions (they have imaginary numbers). Thus we make some new solutions that are linear combinations of these two. They end up looking just like the $Y_{1,0}$ function but oriented differently. The $Y_{1,0}$ function is aligned along the z-axis and we call it p_z , the other two are aligned along x and y and thus are p_x and p_y .

Now for a quandary. We excited the electron in H from its ground state ($n=1, l=0, m=0$) up to a 2p orbital. What shape is the excited state? Is it still spherical? Yes. It has to be. Therefore the best way to think about it is that in the absence of any external perturbation (interaction with something else like a magnetic field or another atom) the electronic is best thought of as being in all three p function at the same time.

Finally, a mistake from class.

At the end of class we looked at the average distance r that the electron is away from the nucleus. This is mostly a function of n . As n increase the average radius r increases. However it is a slight function of l such that for the same n as l increase the average r is slight smaller. Put another way an electron in a 3p function is on average closer to the nucleus than in a 3s. However, I mistakenly suggested that this meant they had different potential energies. This is not the case. They all have the same total energy, the same average potential energy, and the same average kinetic energy.

That is all I can think of for now.