

## 6.A: Solving the Hydrogen Atom (Project)

Enough with pretending atoms are three-dimensional, infinite square wells! It's time to tackle an atom for real. (Before we get too excited, the atom under analysis is hydrogen. All other atoms are impossible to solve analytically.)

### I. Schrödinger's Equation in Spherical Coordinates

The time-independent Schrödinger's equation in Cartesian coordinates is:

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2 \Psi(x, y, z)}{\partial x^2} + \frac{\partial^2 \Psi(x, y, z)}{\partial y^2} + \frac{\partial^2 \Psi(x, y, z)}{\partial z^2} \right) + U(x, y, z) \Psi(x, y, z) = E \Psi(x, y, z) \quad (6.A.1)$$

Of course, this is not really the best coordinate system to use to address the hydrogen atom. A better coordinate system is [spherical coordinates](#). In spherical coordinates, the Schrödinger's equation for the hydrogen atom looks like this:

$$-\frac{\hbar^2}{2m} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \Psi(r, \theta, \phi)}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \Psi(r, \theta, \phi)}{\partial \theta} \right) + \frac{R(r)}{r^2 \sin^2 \theta} \frac{\partial^2 \Psi(r, \theta, \phi)}{\partial \phi^2} \right] + U(r, \theta, \phi) \Psi(r, \theta, \phi) = E \Psi(r, \theta, \phi) \quad (6.A.2)$$

Granted, this doesn't make the equation look very nice, but it makes the solution of the equation possible. If you want to know more about why the spatial derivative part looks like this, go talk to a math professor.

### II. Solving Schrödinger's Equation for Hydrogen

For hydrogen, the potential energy function is simply:

$$U(r, \theta, \phi) = -\frac{ke^2}{r} \quad (6.A.3)$$

Since the potential energy only depends on r, perhaps we can separate the r-dependence in the equation from the angular dependence. Let's assume:

$$\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi) \quad (6.A.4)$$

Substituting these in gives:

$$-\frac{\hbar^2}{2m} \left[ \frac{Y(\theta, \phi)}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R(r)}{\partial r} \right) + \frac{R(r)}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{R(r)}{r^2 \sin^2 \theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} \right] - \frac{ke^2}{r} R(r)Y(\theta, \phi) = ER(r)Y(\theta, \phi) \quad (6.A.5)$$

Next, divide through by the wavefunction,  $R(r)Y(\theta, \phi)$

$$-\frac{\hbar^2}{2m} \left[ \frac{1}{r^2 R(r)} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R(r)}{\partial r} \right) + \frac{1}{r^2 Y(\theta, \phi) \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{1}{r^2 Y(\theta, \phi) \sin^2 \theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} \right] - \frac{ke^2}{r} = E \quad (6.A.6)$$

Move the potential energy to the right side and multiply through by  $\frac{2mr^2}{\hbar^2}$

$$-\left[ \frac{1}{R(r)} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R(r)}{\partial r} \right) + \frac{1}{Y(\theta, \phi) \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{1}{Y(\theta, \phi) \sin^2 \theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} \right] = \frac{2mr^2}{\hbar^2} \left( E + \frac{ke^2}{r} \right) \quad (6.A.7)$$

Move the remaining r-dependence to the right-hand side:

$$-\frac{1}{Y(\theta, \phi) \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) - \frac{1}{Y(\theta, \phi) \sin^2 \theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} = \frac{1}{R(r)} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R(r)}{\partial r} \right) + \frac{2mr^2}{\hbar^2} \left( E + \frac{ke^2}{r} \right) \quad (6.A.8)$$

The left-side of the equation is a function only of  $\theta$  and  $\phi$ , and the right-side is a function only of r. For the two sides to be equal, they must both equal the same constant. Making what may seem like an odd choice for this constant yields two differential equations. The radial equation:

$$\frac{1}{R(r)} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \frac{2mr^2}{\hbar^2} \left( E + \frac{ke^2}{r} \right) = \lambda(\lambda + 1) \quad (6.A.9)$$

and the angular equation:

$$-\frac{1}{Y(\theta, \phi) \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) - \frac{1}{Y(\theta, \phi) \sin^2 \theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} = \lambda(\lambda + 1) \quad (6.A.10)$$

## II.A: The Angular Equation

Re-arranging the angular equation a bit leads to:

$$\sin \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} = -\lambda(\lambda + 1) Y(\theta, \phi) \sin^2 \theta \quad (6.A.11)$$

You may not recognize this equation, but Laplace solved it in 1782 and named the solutions spherical harmonics. Just as sines and cosines can be used to model vibrations in rectangular coordinates (on guitar strings, in 3D infinite wells, etc.) spherical harmonics model vibrations in spherical coordinates. In some sense, you can imagine them as the fundamentally distinct ways in which a spherical surface can vibrate.

Spherical harmonics are labeled by a pair of integers,  $m$  and  $l$ , and typically written as  $Y_{\lambda}^m(\theta, \phi)$

- $m$  is termed the magnetic quantum number and represents the number of complete waves that wrap around the sphere in the azimuthal ( $\phi$ ) direction. Thus, if  $m = 0$ , there is no change as you move around the sphere. If  $m = 1$ , one wavelength wraps around the sphere so that half of the sphere has positive “displacement” and the other half negative.  $m$  can also be negative. In this case, the displacements are flipped, and the “wave” travels the other way around the sphere.
- $l$  is termed the orbital quantum number and controls the polar ( $\theta$ ) direction. The value of  $(l - |m|)$  represents the number of nodes in the polar direction.  $l$  cannot be negative.
- In ye olde fashioned chemistry notation,  $l = 0, 1, 2, 3, \dots$  are referred to as s, p, d, f, ...
- $|m|$  is always less than or equal to  $l$ .

The diagrams below may help you better visualize spherical harmonics. The nodal lines are clearly marked.

1. Draw the nodal lines for the spherical harmonics listed below. Label the sectors + or -.

The first few spherical harmonics are listed below.

$$Y_0^0(\theta, \phi) = \frac{1}{2} \sqrt{\frac{1}{\pi}} \quad (6.A.12)$$

$$Y_1^{-1}(\theta, \phi) = \frac{1}{2} \sqrt{\frac{3}{2\pi}} \sin \theta e^{-i\phi} \quad (6.A.13)$$

$$Y_1^0(\theta, \phi) = \frac{1}{2} \sqrt{\frac{3}{\pi}} \cos \theta \quad (6.A.14)$$

$$Y_1^1(\theta, \phi) = \frac{-1}{2} \sqrt{\frac{3}{2\pi}} \sin \theta e^{i\phi} \quad (6.A.15)$$

$$Y_2^{-2}(\theta, \phi) = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2 \theta e^{-2i\phi} \quad (6.A.16)$$

$$Y_2^{-1}(\theta, \phi) = \frac{1}{2} \sqrt{\frac{15}{2\pi}} \sin \theta \cos \theta e^{-i\phi} \quad (6.A.17)$$

$$Y_2^0(\theta, \phi) = \frac{1}{4} \sqrt{\frac{5}{\pi}} (3 \cos^2 \theta - 1) \quad (6.A.18)$$

$$Y_2^1(\theta, \phi) = \frac{-1}{2} \sqrt{\frac{15}{2\pi}} \sin \theta \cos \theta e^{i\phi} \quad (6.A.19)$$

$$Y_2^2(\theta, \phi) = \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2 \theta e^{2i\phi} \quad (6.A.20)$$

Note lack of node in  $\theta$  direction

Note node at  $\theta = \pi/2$

2. At what values of  $\theta$  does  $Y_2^0(\theta, \phi)$  have nodes?

3.  $Y_3^1(\theta, \phi) = \frac{-1}{8} \sqrt{\frac{21}{\pi}} \sin \theta (5 \cos^2 \theta - 1) e^{i\theta}$ . Where are the nodal lines?

These functions are all normalized so that the integral of  $Y(\theta, \phi)^2$  over the surface of the sphere is 1:

$$\int_0^{2\pi} \int_0^\pi (Y_l^m(\theta, \phi))^2 \sin \theta d\theta d\phi = 1 \quad (6.A.21)$$

4.  $Y_3^{-3} C \sin^3(\theta) e^{-3i\phi}$ . Find C by normalizing this spherical harmonic.

5. Can you see a trend in the spherical harmonics when  $l = |m|$ ? Determine  $Y_5^5(\theta, \phi)$ , including the constant.

#### B. The Radial Equation

Re-arranging the radial equation a bit leads to:

$$\frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \left[ \frac{2mEr^2}{\hbar^2} + \frac{2}{a_0} r - \lambda(\lambda + 1) \right] R(r) = 0$$

If we define  $a_0$ , termed the Bohr radius, as

$$a_0 = \frac{\hbar^2}{mke^2} = 5.29 \times 10^{-11} \text{ m} \quad (6.A.22)$$

then

$$\frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \left[ \frac{2mEr^2}{\hbar^2} + \frac{2}{a_0} r - \lambda(\lambda + 1) \right] R(r) = 0 \quad (6.A.23)$$

Again, you may not recognize this equation, but the 19th century mathematician Leguerre did and the solutions involve *Laguerre polynomials*. These solutions depend on both  $l$  and a new integer,  $n$ .

The radial wavefunction depends on a pair of integers,  $n$  and  $l$ , and is typically written as  $R_{n\lambda}(r)$ .

- All solutions are the product of a polynomial of degree  $(n - 1)$  and the term  $e^{-r/na_0}$ .
- $n$  is termed the principal quantum number and determines the spatial extent of the wavefunction and its energy. Since all solutions drop off as  $r \rightarrow \infty$ , large  $n$  states extend farther from the nucleus.
- The energy of the electron is dependent on  $n$ , and given by the formula:

$$E = -\frac{1}{n^2} \frac{ke^2}{2a_0} = -\frac{13.6 \text{ eV}}{n^2} \quad (6.A.24)$$

- $n$  is greater than zero, and  $l$  is always less than  $n$ .

The first few radial wavefunctions are listed below. (Note  $Z = 1$  for hydrogen)

6. Which of the radial wavefunctions listed above are non-zero at the origin,  $r = 0$ ? In ye olde fashioned chemistry notation, what are these wavefunctions called?

7. Which of the radial wavefunctions listed above have nodes, i.e., radii where the probability of finding the electron is zero? (Do not include  $r = 0$  or  $r = \infty$  as nodes.)

8. Find the nodes for each of the radial wavefunctions listed above, in terms of  $a_0$ .

9. Can you spot a relationship between the number of nodes and the values of  $n$  and  $l$ ? What is it?

These functions are all normalized so that the total probability of finding the electron somewhere is 1. In spherical coordinates, this means:

$$\int_0^\infty (R_{n\lambda}(r))^2 r^2 dr = 1 \quad (6.A.25)$$

10.  $R_{43}(r) = C \left( \frac{r}{a_0} \right)^3 e^{-r/4a_0}$ . Find C by normalizing this radial wavefunction.

The graphic below shows both the radial wavefunction and the radial probability distribution. You should be able to use this to check your node calculations.

Combining the radial wavefunctions with the spherical harmonics generates the complete wavefunction for the electron. If you want to see this in three dimensions, go stand in front of the chemistry labs. If you want to see two dimensional pictures, just look below.

Remember:

- The number of polar nodes is  $l - |m|$
- The number of radial nodes is  $n - (l + 1)$

### III. Angular Momentum

The energy levels for hydrogen are the same as Bohr derived using a much simpler model. (In fact, you reproduced this derivation in the Emission Spectrum laboratory.) However, the angular momentum properties are quite different.

The vector expression for angular momentum is:

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \quad (6.A.26)$$

Thus, a particle circling around the z-axis counter-clockwise would have angular momentum in the +z-direction.

Of course, thinking of the electron as having a well-defined trajectory like this will get you into trouble with Heisenberg.

A better picture would be the one below, at left. In this state, the electron is basically circling around the z-axis, but with quite a bit of “play” in its plane of rotation. We interpret this as the electron’s angular momentum precessing around the z-axis, like a wobbly top. The z-component of its angular momentum is constant, but the total angular momentum vector traces a cone around the z-axis, providing a bit of angular momentum in both the x- and y-directions. Note that  $L_x$  and  $L_y$  are not well-defined like  $L_z$ . They each average to zero but at all times there is some angular momentum in the xy-plane.

Now consider the state at right. You should be able to see that the angular momentum vector lies in the xy-plane, with  $L_z = 0$ . (By the argument above you may believe that it occasionally “wanders” off the xy-plane creating a temporary z-component, which averages to zero, but since  $m = 0$  there is no “wave” encircling the z-axis and hence  $L_z$  is exactly zero.)

Finally, the state at left has no angular momentum at all. The probability “cloud” is completely independent of both  $\phi$  and  $\theta$  so there is no “motion” in any angular direction.

Rather than examining the wavefunction for every possible situation conceptually, I’m now just going to tell you the formulas for the total angular momentum and the z-component of angular momentum:

$$|L| = \sqrt{\lambda(\lambda + 1)} \hbar \quad (6.A.27)$$

$$L_z = m \hbar \quad (6.A.28)$$

When no external electric or magnetic fields are present, the allowed energy levels do not depend on the angular momentum state. For each value of  $l$ , there are  $(2l + 1)$  degenerate energy states.

In the  $l = 2$  states illustrated at right, the magnitude of the angular momentum is always

$$|L| = \sqrt{2(2 + 1)} \hbar = 2.44 \hbar \quad (6.A.29)$$

This represents the length of the vector precessing around the z-axis. The projection of this vector on the z-axis can take on one of five different values determined by  $m$ . With no external field to break the  $\pm z$ -symmetry all five of these states have the same energy.

11. For each of the five states above, determine the angular momentum in the xy-plane.

All this talk about precessing around the z-axis may have you convinced that at any particular moment we can determine the exact direction of and therefore calculate not only the amount of angular momentum in the xy-plane, but the exact components in both x and y. However, if this was true (i.e., if we knew  $L_x$ ,  $L_y$ , and  $L_z$  at the same time) it would mean we know both the position and linear momentum of the electron at the same time. Again, Heisenberg wouldn’t like this! We need to think of the electron “cloud” as somehow precessing around the z-axis, with no definite direction at any particular time.

12. Consider the  $n = 4$  state. What is the total degeneracy of this state? (Do not include electron spin.) List the angular momentum and  $z$ -component of angular momentum for each sub-state.

It may confuse you for me to say that all of the states above (4s, 4p, 4d, and 4f in chemistry notation) have the same energy, but for hydrogen they do. However, you've learned in chemistry that these states have different energies and are thus filled in a specific order. That's only the case for multi-electron atoms. Basically, if you incorporate the interactions of all the electrons the degeneracy between these states splits.

For example,  $s$ -state electrons have a radial wavefunction that is non-zero at the location of the nucleus while the other states don't. Thus, when the  $s$ -state electrons are closer to the nucleus than the other states, they effectively "screen" the nuclear charge so that the other states "see" less positive charge. This makes the other states less tightly bound. If there are  $Z$  protons in the nucleus,  $s$ -state electrons interact with all  $Z$  protons while  $p$ -states only "see" approximately  $Z - 2$  protons,  $d$ -states "see"  $Z - 8$ , etc. This effect, electron screening, and other electron-electron interactions split the degeneracy present for a single-electron atom.

## IV. Emission Spectrum

### IV.A: Selection Rules

In the Bohr model of hydrogen, the emission spectrum is simple. Every time the electron drops from a higher to a lower energy level a photon is emitted with energy equal to the difference between these levels. However, the real situation is more complicated. One reason is that the photon has angular momentum.

Since the photon has angular momentum, and angular momentum is conserved, the atom can only undergo photon emission if the total angular momentum of the atom changes. This requirement creates a selection rule:

$$\Delta l = \pm 1 \quad (6.A.30)$$

The angular momentum carried away by the photon can either come from the  $z$ -component or the  $xy$ -plane component:

$$\Delta m = 0, \pm 1 \quad (6.A.31)$$

Thus,  $s$ -states cannot decay to  $s$ -states,  $p$ -states cannot decay to  $p$ -states, etc. Some allowed transitions are illustrated at right.

13. Consider the state (4,1,1). List all decays from this state that are "allowed" by the selection rules above.

Decays that do not obey the selection rules above are not strictly forbidden, they just occur at greatly reduced rates.

### IV.B: Zeeman Effect

Another complication to the simple emission spectrum described by Bohr occurs if the atom is in the presence of an external magnetic field, which for convenience we will imagine as oriented in the  $z$ -direction.

If  $m$  is not equal to 0, we can imagine the electron as orbiting around the  $z$ -axis. This orbiting electron creates a magnetic field that interacts with the external magnetic field. If these two fields are in opposite directions the electron "wants" to flip over and align with the external field. This can be quantified as an additional source of potential energy given by:

$$U = m\mu_B B \quad (6.A.32)$$

where  $\mu_B$  is the Bohr Magnetron, defined as

$$\mu_B = \frac{e\hbar}{2m} \quad (6.A.33)$$

$$\mu_B = 5.79 \times 10^{-5} \text{ eV/T} \quad (6.A.34)$$

Imagine the 2p state illustrated at right in the presence of a magnetic field in the  $+z$ -direction. If the electron is orbiting counterclockwise ( $m = 1$ ) it creates a magnetic field oriented in the  $-z$ -direction, since it is negatively charged. Since these fields have opposite orientation, this electron state has additional potential energy. The opposite is true for the  $m = -1$  state. The  $m = 0$  is unaffected by the magnetic field. Thus, the threefold degeneracy in the 2p state is broken in the presence of a magnetic field.

Due to this breaking of the energy degeneracy of 2p, rather than a single emission line corresponding to the 2p to 1s transition there are three closely spaced emission lines. This splitting of spectral lines due to the presence of an external magnetic field is termed the *Zeeman effect*.

14. Consider the 2p state in the presence of a 2.0 T magnetic field. If this state decays to the 1s state, find the shift in wavelength of the  $m = \pm 1$  states relevant to the  $m = 0$  state. What is this shift as a percentage of the original wavelength?

### C. Intrinsic Spin

One last complication, I promise.

The angular momentum we have been discussing up to this point is termed orbital angular momentum and is due, not surprisingly given its name, to the orbital motion of the electron. In addition, the electron has an intrinsic angular momentum, commonly referred to as spin. This angular momentum is not really due to the electron “spinning” in space but rather represents a fundamental characteristic of the electron, like its charge or its mass.

The electron’s spin vector adds to its orbital angular momentum vector to form its total angular momentum vector, . All of these vectors may precess around the z-axis.

The spin vector obeys similar mathematics to the angular momentum vector, although the spin quantum number,  $s$ , is always equal to  $\frac{1}{2}$ .

If you are following along you should now expect me to discuss how the z-portion of the spin can interact with an external magnetic field to further split each sub-state into two different energy levels, a spin-up and a spin-down sub-state. In fact, there is a splitting involving a potential energy term given by:

$$U = \pm \mu_B B \quad (6.A.35)$$

However, this splitting is not due to an external magnetic field but rather the magnetic field generated by the electron’s own orbital motion. If  $L_z$  and  $S_z$  are in the same direction (either both “up” or both “down”) the potential energy is positive while if they are in opposite directions the potential energy is negative. This interaction between the spin and angular momentum is termed spin-orbit coupling. The difference between these levels is given by:

$$\Delta E = E_{\text{parallel}} - E_{\text{antiparallel}} = \frac{mc^2 \alpha^4}{n^5} \quad (6.A.36)$$

where  $\alpha$ , the fine structure constant, is very close to  $1/137$ .

15. Consider the (2,1,1) state with no external magnetic field. If this state decays to the 1s state, find the shift in wavelength of the LS-parallel state with the LS-antiparallel state. What is this shift as a percentage of the original wavelength?

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