

## Schrödinger, 4

### The sanitized hydrogen atom: separating the variables

Separation of variables in the Schrödinger Equation for the hydrogen problem requires expressing  $\Psi$  as a product,  $\Psi(r, \theta, \phi, t) = R(r)\Theta(\theta)\Phi(\phi)T(t)$ , substituting into the partial differential equation [(5) in Sc3], and then dividing by  $\Psi$ . As in the square well problems, the separation constant for the  $t$  part of the separation is the particle's eigen-energy,  $E$ . The rest of the resulting equation is

$$E = -\frac{\hbar^2}{2m} \left\{ \frac{1}{R} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{1}{r^2} \left[ \frac{1}{\Theta} \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\sin^2 \theta} \left( \frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} \right) \right] \right\} - \frac{k_E e^2}{r}. \quad (1)$$

While this looks unpromising in terms of separation (because all the coordinates are still scrambled together), pieces can be attacked sequentially starting with the term  $\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2}$ . This term contains the only  $\phi$  dependence and therefore must be constant. Let's call the constant of separation of  $\phi$  from the other variables  $-k_\phi^2$ . Setting  $\frac{d^2 \Phi}{d\phi^2} = -k_\phi^2 \Phi$  (to make the equation look like a harmonic oscillator) and solving, leads to  $\Phi = A_\phi e^{\pm i k_\phi \phi}$ , where  $A_\phi$  is a constant. If we imagine starting at some value of  $\phi$  and going around the  $z$ -axis by  $2\pi$  we should get exactly the same wavefunction back, so  $k_\phi$  **must be an integer (including zero)**—conventionally denoted  $m_l$ . (Keep in mind that  $m_l$  is a dimensionless integer, not a mass.) It is customary to use just the positive sign in  $e^{\pm i m_l \phi}$  and take care of the minus by letting  $m_l$  be either positive or negative.

The stuff in the square brackets on the right-hand side of the separation equation is now  $\left[ \frac{1}{\Theta} \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \frac{1}{\sin^2 \theta} (-m_l^2) \right]$ , which only depends on  $\theta$ . Since this is the only place  $\theta$  appears, this term must equal another constant. Call it  $-k_\theta^2$ . This leads to the decidedly un-harmonic oscillator looking equation

$$\sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) = (m_l^2 - k_\theta^2 \sin^2 \theta).$$

For reasons similar to the argument above for  $\phi$ , however (and exploiting a bit of arcane 19<sup>th</sup> century mathematics), it turns out that  $k_\theta^2$  is also an integer, but now with the form  $k_\theta^2 = l(l+1)$ , where  $l$  **can be 0, 1, 2, ...**. The smoothness requirement for the angular wavefunctions introduces an additional constraint, namely, that  $-l \leq m_l \leq l$ . That is, **for every value of  $l$  there are  $2l+1$  possible  $m_l$  values:**  $-l, -l+1, \dots, -1, 0, 1, \dots, l-1, l$ .

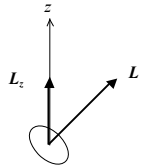
Finally, we have

$$ER = -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{\hbar^2 l(l+1)}{2mr^2} R - \frac{k_E e^2}{r} R. \quad (2)$$

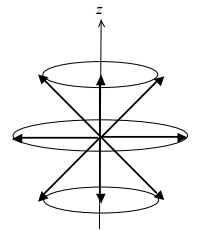
In (2), the variables  $t, \theta, \phi$  have all been separated out leaving only  $r$ . Note that the second term on the right hand side of (2) arises from the angular derivatives in (1) which in Sc3 were

identified with the square of the orbital angular momentum. Because it involves the integer  $l$ , it is apparent that the magnitude of the orbital angular momentum is quantized—i.e., it can't take on just any values. (Remember: this is due to the requirement that the wavefunction has to be smoothly continuous.) Indeed,  $L_{op}^2 \Psi = L^2 \Psi = \hbar^2 l(l+1) \Psi$ , where  $L$  is the magnitude of the angular momentum eigenvalues:  $L = \hbar \sqrt{l(l+1)}$ , with allowed values  $0\hbar, \sqrt{2}\hbar, \sqrt{6}\hbar, \sqrt{12}\hbar$ , and so on.

The operator  $\hbar^2 \partial^2 / \partial \phi^2$  is part of  $L_{op}^2$ ; it refers to motion around the  $z$ -axis and is therefore called  $L_{z,op}^2$ . The eigenvalues of  $L_{z,op}$ , namely  $\hbar m_l$ , deal with the allowed “orientations” of an orbit. To the right is a picture of a classical circular orbit tipped so that its angular momentum vector is *not* along  $z$ . The magnitude of the angular momentum,  $L = \hbar \sqrt{l(l+1)}$ , is greater than the magnitude of its projection along  $z$  (i.e.,  $|L_z|$ ). The angle between  $z$  and the angular momentum vector is given by  $\cos^{-1}(L_z/L)$ . For the quantized angular momenta described above this angle is given by one of the  $2l+1$  possible values,  $\cos^{-1}[m_l / \sqrt{l(l+1)}]$ . The requirement that the wavefunction be smoothly continuous forces the orbital angular momentum vector to have only certain allowed magnitudes and to point in only certain allowed directions!



**Example:** If  $l=1$  (or  $\sqrt{l(l+1)} = \sqrt{2}$ ) the  $2 \cdot 1 + 1 = 3$  possible angles are  $45^\circ$  (for  $m_l = 1$ ),  $90^\circ$  (for  $m_l = 0$ ), and  $135^\circ$  (for  $m_l = -1$ ). This is shown to the right. The angular momentum vector has magnitude  $\hbar \sqrt{2}$ , but it can't point in any direction. Its tip can only be on one of the three circles shown, so that the projections along  $z$  are  $\pm \hbar$  or  $0$ .



Note that there is *no* absolute  $z$ -axis in space. In order to make a measurement of angular momentum orientation, you have to do something such as turn on a magnetic field. Once you do that then  $z$  is established by the field direction. Note also, that **because the Coulomb potential energy is spherically symmetric the electron's total energy is independent of orbital orientation**. Thus, for any value of  $l$  there are  $2l+1$   $m_l$  states with the same energy; this is a case of *real degeneracy*.

### Sanitized hydrogen energy eigenvalues

The electron wavefunction in the H-atom does not go abruptly to zero at some finite radius. In fact, there are two qualitatively different possibilities corresponding to the total energy being positive or negative. When the electron's total energy is positive, the wavefunction extends to  $r = \text{infinity}$  and describes an unbound electron capable of escaping the pull of the proton. When the electron's total energy is negative, however, the attraction of the proton wins out over the electron's desire to escape and the electron is trapped near the proton, with a wavefunction that rapidly goes to zero as  $r$  increases. The allowed energy eigenstates in this case are called “bound” states. Here, we focus on these.

Equation (2) has an effective potential energy due partly to the real Coulomb attraction and partly from the (fictitious) centrifugal repulsion:  $U_{\text{effective}} = \frac{\hbar^2 l(l+1)}{2mr^2} - \frac{k_E e^2}{r}$ . For a *classical*

particle, the radius where the effective potential energy is minimum (i.e., set the derivative of  $U_{\text{effective}}$  to zero and solve for  $r$ ) would correspond to a classical circular orbit with

$r_* = \frac{\hbar^2}{mk_E e^2} l(l+1)$ . Though the quantum mechanical version of hydrogen is hardly classical, the

factor  $a_0 = \frac{\hbar^2}{mk_E e^2}$  has the dimensions of length and its value sets the length or size scale of the

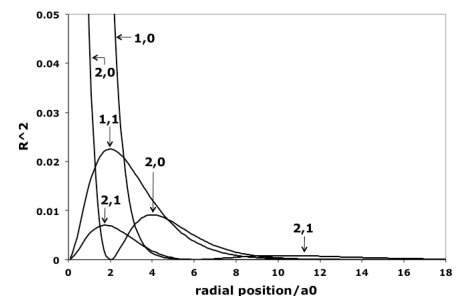
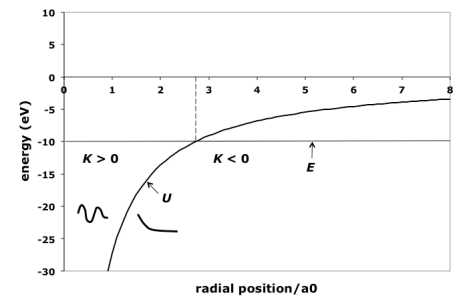
atom. For historical reasons, it's called the "Bohr radius" and has the value 0.0529 nm (i.e., about 1/20 nm). Plugging  $r_* = a_0 l(l+1)$  into  $U_{\text{effective}}$  produces

$U_{\text{effective}} = \left( \frac{\hbar^2}{2ma_0^2} - \frac{k_E e^2}{a_0} \right) \frac{1}{l(l+1)} = -\frac{\hbar^2}{2ma_0^2} \frac{1}{l(l+1)}$ . The factor  $E_0 = \frac{\hbar^2}{2ma_0^2} = 13.6 \text{ eV}$  sets the scale

of electronic energy in the hydrogen atom. The length and energy scales of the hydrogen problem are fixed by the mass and charge of the electron, the charge of the proton, the strength of the Coulomb force, and the fundamental constant  $\hbar$ , and nothing else. As noted previously, there actually can be no classical circular orbits because that would require fixing the electron's radial momentum to be zero while also fixing its radial position to be  $r_*$ , which violates the

uncertainty principle. In addition, the Schrödinger Equation permits stable  $l = 0$  states (in which the electron effectively "passes through" the proton), which are not permitted classically. Thus, a careful analysis of the solutions of (2) is required to understand the allowed states of motion of the electron. Regardless of details, however, the extent of the wavefunctions and the corresponding energies will be related to  $a_0$  and  $E_0$ , respectively.

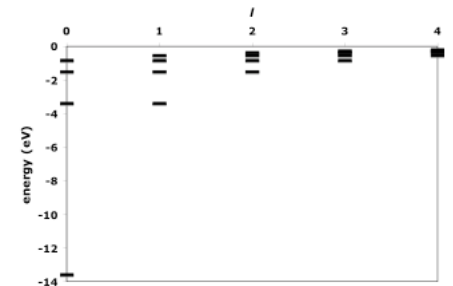
Like the finite square well, the Coulomb potential energy is "softer" than an infinite well potential energy, and, as a result, the electron wavefunction can leak out into the region where the classical kinetic energy would have to be negative. That's shown in the figure to the right. Recall that kinetic energy = (total energy – potential energy). When kinetic energy is positive (as to the left of the dotted line in the figure) the wavefunction wiggles; when the kinetic energy is negative the wavefunction has to die off exponentially (to the right of the dotted line). The allowed energy eigenvalues are those for which the wiggles and die-offs match smoothly where  $K = 0$ . As in the finite square well, the hydrogen radial wavefunction only smoothly matches, for a given value of  $l$ , for certain wobble shapes; these are enumerated by a positive integer  $n_r$  ( $= 1, 2, 3, \dots$ ). Like the quantum number associated with energy eigenfunctions in the finite square well, the hydrogen radial quantum number  $n_r$  counts the number of maxima in  $R^2$  between  $r = 0$  and where the die-off starts. The figure to the right shows a few values of  $R_{n_r, l}^2$ . The pairs of numbers correspond to  $n_r$  and  $l$ , respectively. Notice that when  $n_r = 1$  there is one maximum, when  $n_r = 2$ , there are two. Also, notice that  $R_{n_r, l}^2$  is large at the origin when  $l = 0$ , and zero there when  $l \neq 0$ .



The energy eigenvalues for the sanitized hydrogen atom are

$$E_{n,l} = -\frac{\hbar^2}{2ma_0^2} \frac{1}{(n_r + l)^2} = -E_0 \frac{1}{(n_r + l)^2}. \quad (3)$$

The energy level diagram to the right shows energies for different combinations of  $l$  and  $n_r$ . The rules are that  $n_r$  can be any positive integer and that  $l$  can be 0 or any positive integer. Below each  $l$  is a set of energies, one for each value of  $n_r = 1, 2, 3, \dots$  (increasing upwards). In each case the lowest energy (most negative) corresponds to  $n_r = 1$ , the next to  $n_r = 2$ , and so on. The level



$E_{10} = -13.6\text{eV}$  is the lowest allowed energy (the ground state). Levels  $E_{20}$  and  $E_{11}$  are degenerate (with energy =  $-3.4\text{ eV}$ ). Levels  $E_{30}$ ,  $E_{21}$ , and  $E_{12}$  are also degenerate (with energy =  $-1.51\text{ eV}$ ). And so on. These degeneracies are accidents of how the energies are calculated algebraically. The levels also have “real” degeneracy, because each  $l$  has  $2l+1$   $m_l$  states all with the same energy.

Because  $l$  and  $n_r$  can take on all integer values their sum can also. **The standard convention is to set  $n_r + l$  equal to a “principal quantum number”  $n = 1, 2, 3, \dots$  with**

$E_n = -\frac{13.6\text{eV}}{n^2}$ , **and with the additional rule that for a given  $n$ ,  $l = 0, 1, \dots, n-1$ .** This way of

doing things obscures the fact that energy is built of a radial part and an angular part, and makes it seem like angular momentum is somehow restricted by the quantum number  $n$ . Nonetheless, this scheme is widely used and we just have to deal with it. The diagram above is exactly the same when  $n$  is used, but we have to remember that  $n = 2$  is the lowest value for the  $l = 1$  column,  $n = 3$  is the lowest for the  $l = 2$  column, and so forth. Even more obscurely, the states using  $n$  are usually represented by a number (that is,  $n$ ) next to a letter supposedly representing angular momentum. The letters follow a historical precedent:

$l = 0 \leftrightarrow s, l = 1 \leftrightarrow p, l = 2 \leftrightarrow d, l = 3 \leftrightarrow f$ . After  $f$  the letters just follow the alphabet, that is,  $g, h, i$ , etc. Thus, using this convention in the diagram above, the ground state is labeled 1s; the first excited state with  $l = 0$  is 2s; the state degenerate with 2s with  $l = 1$  is 2p. The degenerate states with the next higher energy are 3s, 3p, and 3d, and so on. If we add up all the degeneracies (including those associated with  $m_l$ ) we find the total degeneracy of any level labeled by  $n$  is  $n^2$ .

Finally, note that if  $E > 0$ , all wiggles are possible (no matching is required) so that any positive energy is allowed. The wavefunctions for these energies spread out to  $r = \text{infinity}$ , implying that the electron can be found at any distance from the proton. These are “unbound” states. It takes a minimum of 13.6 eV to promote a 1s electron to an unbound state. This is the so-called “ionization energy” for a hydrogen atom.