

# The Hydrogen Atom

Lecture 24

Physics 342  
Quantum Mechanics I

Monday, March 29th, 2010

We now begin our discussion of the Hydrogen atom. Operationally, this is just another choice for spherically symmetric potential (i.e. Coulomb). Morally, of course, this is one of the great triumphs of our time (technically, the time two before ours). We already know the angular solutions, the usual  $Y_\ell^m(\theta, \phi)$ , so all we need to do is establish the radial portion of the wavefunction, and put it all together. Notice that we are following Professor Griffiths' treatment here, and he uses a different initial dimensionless length than you did for your homework. This is no problem, in the end, the spectrum has to be the same no matter which choice one makes. You will see a slight difference in the recursion relation, and since the recursion relation in this case is more directly related to the associated Laguerre definition, it is somewhat easier to get the actual radial wavefunctions here.

## 24.1 Radial Wavefunction

The potential, in this case, represents the electrostatic field set up by the nucleus of the Hydrogen atom, as felt by the electron:

$$U(r) = -\frac{e^2}{4\pi\epsilon_0 r}. \quad (24.1)$$

This goes into the usual (with  $u(r) = rR(r)$  as before)

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[ U(r) + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} - E \right] u = 0 \quad (24.2)$$

where we are associating  $m$  with the mass of the electron. We just made a pretty dramatic approximation. We know that the two-particle problem can

be reduced to a stationary center, provided we use the reduced mass of the system. On the one hand, that is fine – but on the other: What do we mean by a two-particle problem in quantum mechanics? For now, just imagine the nucleus doesn't have much “kinetic” energy, so that it remains pretty much fixed (what about the energy associated with having it around at all? Its relativistic “rest energy” is still there, but we are not doing relativistic quantum mechanics yet).

If we write the above out, we have:

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[ -\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} - E \right] u = 0. \quad (24.3)$$

As with the infinite square well, it makes sense to let  $\kappa = \frac{\sqrt{-2mE}}{\hbar}$  (negative inside the square root, now – bound states will have  $E < 0$  and we want to make  $\kappa$  real). We want to define a new “coordinate”  $\rho \equiv \kappa r$ . The advantage is to render the coordinate variable itself unitless. Whenever we want to consider limiting cases of an equation or more generally, a physical setting, we need a point of comparison.

What does it mean to be “far away” from a distribution of charge, for example? That clearly depends on how large the distribution itself is. By re-parametrizing using a fundamental length in the problem, we have allowed for easier classification of limits. For example, on the E&M side, suppose we have a dipole moment with a certain length  $d$ . Then “far away” means that a field point at a distance  $r$  from the origin is large compared to  $d$ :  $r \gg d$ . Now suppose we wrote everything in our problem in terms of the new length  $\tilde{r} \equiv r/d$ . We have eliminated the explicit comparison with  $d$  and can refer to “small  $\tilde{r}$ ” unambiguously as  $\tilde{r} \sim 0$ , making for easier Taylor expansion, etc.

The point is,  $\kappa$  has units of 1/length and involves the fundamental (and as yet unknown) energy scale, it is a natural choice for constructing  $\rho = \kappa r$ , a unitless quantity. In the above, we just replace  $r \rightarrow \rho/\kappa$ , and  $\frac{d}{dr} \rightarrow \kappa \frac{d}{d\rho}$ . Performing this simple change of variables, multiplying by  $\frac{2m}{\hbar^2}$  in the process, we have

$$-\frac{d^2 u(\rho)}{d\rho^2} + \left[ -\frac{m e^2}{2\pi\epsilon_0 \hbar^2 \kappa \rho} + \frac{\ell(\ell+1)}{\rho} + 1 \right] u(\rho) = 0. \quad (24.4)$$

We have another scale defined by  $\rho_0 \equiv \frac{m e^2}{2\pi\epsilon_0 \hbar^2 \kappa}$  (there are, evidently, two energy scales of interest to us here, hence two lengths – we could have written

$\rho$  in terms of  $\rho = (\rho_0 \kappa) r$ , and with this, we can write the final form:

$$\frac{d^2 u}{d\rho^2} = \left[ 1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2} \right] u. \quad (24.5)$$

As for limiting cases, we can take  $\rho \rightarrow \infty$ , which gives us growing and decaying exponentials as solutions:

$$\frac{d^2 u}{d\rho^2} = u \rightarrow u(\rho) = A e^{-\rho} \quad (24.6)$$

where we have thrown out the growing exponential, that will not be normalizable.

On the other hand, when the barrier-term dominates, for small  $\rho$ , we have (using  $\bar{u}$  to distinguish from the actual solution)

$$\frac{d^2 \bar{u}}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2} \bar{u}, \quad (24.7)$$

and we can solve this by consider a generic polynomial (always a good ansatz for ODE's of the above flavor):  $\bar{u}(\rho) = a \rho^p$ , then

$$a p(p-1) \rho^{p-2} = a(\ell(\ell+1)) \rho^{-2} a \rho^p \quad (24.8)$$

and then we have a solution for  $p(p-1) = \ell(\ell+1)$ , or  $p = -\ell$ ,  $p = \ell+1$ . The general solution is a linear combination:

$$\bar{u}(\rho) = a \rho^{-\ell} + b \rho^{\ell+1} \quad (24.9)$$

and we set  $a = 0$ , for  $\rho$  near zero, this will blow up.

Finally, we will use these two regimes to factor the full solution – take

$$u(\rho) = \rho^{\ell+1} e^{-\rho} v(\rho), \quad (24.10)$$

this is naturally dominated by the polynomial near  $\rho \sim 0$ , and the exponential will help with integration at infinity. If we input this into our differential equation, we get

$$\rho \frac{d^2 v}{d\rho^2} + 2(\ell+1-\rho) \frac{dv}{d\rho} + (\rho_0 - 2(\ell+1)) v = 0. \quad (24.11)$$

Let  $x \equiv 2\rho$ , then in terms of  $x$ , the above is

$$x \frac{d^2 v}{dx^2} + (2(\ell+1) - x) \frac{dv}{dx} + \left( \frac{1}{2} \rho_0 - (\ell+1) \right) v = 0. \quad (24.12)$$

Now, the differential equation:

$$x \frac{d^2}{dx^2} L_n^k(x) + (k+1-x) \frac{dL_n^k(x)}{dx} + n L_n^k(x) = 0 \quad (24.13)$$

has solutions  $L_n^k(x)$ , the “associated Laguerre polynomials”, for integer  $n$ . This is almost the above, if we set  $k+1 = 2(\ell+1)$  and  $n = (\frac{1}{2}\rho_0 - (\ell+1))$  – and we assume that  $n$  is an integer. In that case, the solution to our problem is just:

$$v(x) = L_{\frac{1}{2}\rho_0 - (\ell+1)}^{2\ell+1}(x), \quad (24.14)$$

This pre-supposes that  $\frac{1}{2}\rho_0 \equiv \bar{n}$  is an integer, but we can return to that later on. For now, this is the source of the quantization of energy, since we have:

$$2\bar{n} = \rho_0 = \frac{m e^2}{2\pi\epsilon_0 \hbar^2 \kappa} = \frac{m e^2}{2\sqrt{2}\epsilon_0 \hbar \sqrt{-E m \pi}} \longrightarrow E = -\frac{m e^4}{32\epsilon_0^2 \hbar^2 \pi^2 \bar{n}^2}, \quad (24.15)$$

or in more standard form, labelled using  $n$  the “principal quantum number”:

$$E_{\bar{n}} = -\left(\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right) \frac{1}{\bar{n}^2} \equiv \frac{E_1}{\bar{n}^2}. \quad (24.16)$$

This is the energy spectrum of Hydrogen – we shall return to it in a moment.

## 24.2 Associated Laguerre Polynomials

The associated Laguerre polynomials are defined as the solution to the above differential equation (24.13). Most special functions arise as solutions to “difficult” ODEs, meaning ones not solvable by exponentials or polynomials. The solutions usually proceed by series expansion (Frobenius’ method), and involve points at which we remove certain elements of the solution with behaviour we do not want to allow. The associated Laguerre polynomials have Rodrigues formula<sup>1</sup>

$$L_n^k(x) = \frac{e^x x^{-k}}{n!} \frac{d^n}{dx^n} \left( e^{-x} x^{n+k} \right) \quad (24.17)$$

and can be related to the Laguerre polynomials via

$$L_n^k(x) = (-1)^k \frac{d^k}{dx^k} L_{n+k}(x) \quad (24.18)$$

<sup>1</sup>For a further compilation of properties, see Arfken and Weber, p. 832.

Because it is the “integerization” of  $\rho_0$  that quantizes the energy in the Hydrogen atom, it is worthwhile to generate the series solution and see how this appears effectively as a *boundary condition* (vanishing of the radial wavefunction at infinity). We’ll return to the direct ODE,

$$\rho \frac{d^2 v}{d\rho^2} + 2(\ell + 1 - \rho) \frac{dv}{d\rho} + (\rho_0 - 2(\ell + 1)) v = 0, \quad (24.19)$$

and make the series ansatz:

$$\begin{aligned} v(\rho) &= \sum_{j=0}^{\infty} c_j \rho^j \\ v'(\rho) &= \sum_{j=0}^{\infty} c_j j \rho^{j-1} \\ v''(\rho) &= \sum_{j=0}^{\infty} c_j j(j-1) \rho^{j-2}. \end{aligned} \quad (24.20)$$

The relevant terms from the ODE are:

$$\begin{aligned} \rho v''(\rho) &= \sum_{j=0}^{\infty} c_j j(j-1) \rho^{j-1} = \sum_{k=-1}^{\infty} c_{k+1} k(k+1) \rho^k \\ &= \sum_{k=0}^{\infty} c_{k+1} k(k+1) \rho^k \\ 2(\ell + 1) v'(\rho) &= \sum_{j=0}^{\infty} c_j j 2(\ell + 1) \rho^{j-1} = \sum_{k=-1}^{\infty} c_{k+1} (k+1) 2(\ell + 1) \rho^k \\ &= \sum_{k=0}^{\infty} c_{k+1} (k+1) 2(\ell + 1) \rho^k \\ -2\rho v'(\rho) &= \sum_{k=0}^{\infty} c_k k(-2) \rho^k \\ (\rho_0 - 2(\ell + 1)) v(\rho) &= \sum_{k=0}^{\infty} c_k (\rho_0 - 2(\ell + 1)) \rho^k \end{aligned} \quad (24.21)$$

where we have set  $k = j - 1$  in the first two expressions, and noted that, for each, the  $k = -1$  term vanishes anyway.

Now we just read down the list to get the recursion relation:

$$c_{k+1} (k(k+1) + 2(k+1)(\ell+1)) - c_k (2k - \rho_0 + 2(\ell+1)) = 0 \quad (24.22)$$

holds for all  $\rho^k$ . Solving for  $c_{k+1}$ :

$$c_{k+1} = \frac{2(k+\ell+1) - \rho_0}{(k+1)(k+2(\ell+1))} c_k. \quad (24.23)$$

This can clearly be used to find all the coefficients given just the first one,  $c_0$ . But if we think about the large- $k$  limit, large values of  $\rho$  dominate the expansion ( $\rho^{100} \gg \rho^2$  for  $\rho > 1$ , for example), then we have

$$c_{k+1} \sim \frac{2}{k+1} c_k. \quad (24.24)$$

Now, if this had been the recursion relation all along (meaning, for all orders), we would have had:

$$c_k = \frac{2^k}{k!} c_0 \longrightarrow \sum_{k=0}^{\infty} c_k \rho^k = \sum_{k=0}^{\infty} c_0 \frac{2^k}{k!} \rho^k = c_0 e^{2\rho}, \quad (24.25)$$

where we recognize the Taylor expansion for the growing exponential. This is a manifestation of a solution that lurks in (24.19) in the large- $\rho$  limit, where it is effectively just  $v''(\rho) - 2v'(\rho) = 0$ , meaning that  $v(\rho) = \alpha e^{2\rho} + \beta$ . What we want to do is kill the growing exponential term, which will overwhelm the  $e^{-\rho}$  we have already factored out of the radial  $u(r)$  solution. To accomplish this, we must truncate the series, eliminating, “by hand” the growing solution. Truncation is simple, we just need  $c_{\bar{k}+1} = 0$  for some integer  $\bar{k}$ , then all successive coefficients are also zero by the recursion formula.

Define  $\bar{k}$  from (24.23):

$$2(\bar{k} + \ell + 1) - \rho_0 = 0, \quad (24.26)$$

and there we have it –  $\rho_0$  must be an integer if it is to kill the integer  $2(\bar{k} + \ell + 1)$ . This makes our  $\rho_0 = 2n$  critical value clear:  $n$  defines the value of  $\rho_0$  which will cause the series to truncate:

$$n = \bar{k} + \ell + 1. \quad (24.27)$$

For a given  $n$ , now, which is the direction we are interested in, we can find  $\bar{k}$  for a given  $\ell$  from the above. What is interesting is that the energies

themselves are indexed only by  $n$ , so we can ask: “How many states are there with an energy  $E_n$  for given  $n$ ?” The answer is simple – we have  $\bar{k} = n - (\ell + 1)$ , and the lower limit on the “cutoff” is  $\bar{k} = 0$  so  $\ell = n - 1$ . The smallest value for  $\ell$  is zero, so  $\bar{k} = n - 1$  is the max. Then  $\ell = 0 \dots n - 1$  are the allowed values. But let’s not forget, in our state counting, the  $m = -\ell \dots \ell$  angular portion – there are  $2\ell + 1$  states with a given value of  $\ell$ , so the total number of states with energy  $E_n$  is:

$$\sum_{\ell=0}^{n-1} (2\ell + 1) = n^2 \quad (24.28)$$

this is the *degeneracy* of the Hydrogenic states.

## 24.3 Hydrogen Physics

What we have, then, is a quantized energy:

$$E_n = \frac{E_1}{n^2} \quad E_1 \equiv -\left(\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right) \quad (24.29)$$

shared by  $n^2$  states. Because we scaled the radial coordinate  $r$  by the energy, effectively, we have  $n$ -dependent scaling:  $\rho = \kappa r = \frac{\sqrt{-2mE_n}}{\hbar} r$  and we can write this naturally in terms of a characteristic length – that of the ground state:

$$\kappa r = \frac{\sqrt{-2mE_1}}{\hbar n} r = \frac{m e^2}{4\pi\epsilon_0 \hbar^2} \frac{r}{n} \equiv \frac{r}{a n} \quad (24.30)$$

with  $a = \frac{4\pi\epsilon_0 \hbar^2}{m e^2} = 0.528 \times 10^{-10}$  m, the “Bohr radius” of Hydrogen (half an Angstrom). Using this for  $\rho$ , and normalizing the associated Laguerre polynomials, we have the full time-independent solution:

$$\psi_{n\ell m}(r, \theta, \phi) = \sqrt{\left(\frac{2}{a n}\right)^3 \frac{(n - \ell - 1)!}{2n((n + \ell)!)^3}} \left(e^{-\frac{r}{a n}}\right) \left(\frac{2r}{a n}\right)^\ell \left(L_{n-\ell-1}^{2\ell+1}(2r/(a n))\right) Y_\ell^m(\theta, \phi). \quad (24.31)$$

In particular, the ground state, with  $n = 1, \ell = m = 0$  has

$$\psi_{100} = \frac{1}{\sqrt{\pi a^3}} e^{-\frac{r}{a}} \quad (24.32)$$

with energy:

$$E_1 = -\left(\frac{m}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right) = -13.6 \text{ MeV}. \quad (24.33)$$

### 24.3.1 Electric field of the Ground State

One of the advantages of a quantum mechanical description of things like the electron is that they tend to “smear out” point effects. For example, the charge density of a point electron is, of course,  $\rho(\mathbf{r}) = q \delta(\mathbf{r})$ , and its field is singular “at” the electron,  $\mathbf{E} = \frac{q}{4\pi\epsilon_0 r^2} \hat{\mathbf{r}}$ . If we think of the “charge density” of the electron in the ground state of Hydrogen, then

$$\rho(\mathbf{r}) = q |\psi_{100}|^2 = \frac{q}{\pi a^3} e^{-\frac{2r}{a}}. \quad (24.34)$$

We take this with a grain of salt, of course – this is the probability per unit volume of finding the charge at radius  $r$ , so while we can think of the electron as a “cloud”, it’s not exactly the same as a known distribution of charge. Still, we can calculate the electric field associated with this as if it *were* a distribution of charge. Gauss’ law gives:

$$\int \mathbf{E} \cdot d\mathbf{a} = \frac{Q_{enc}}{\epsilon_0} = 4\pi \int_0^r \frac{q}{\pi a^3} e^{-2r/a} r^2 dr, \quad (24.35)$$

and making the usual spherical ansatz, we have  $\mathbf{E} = E(r) \hat{\mathbf{r}}$ , so that

$$4\pi r^2 E = \frac{q}{\epsilon_0 a^2} \left( a^2 - e^{-2r/a} (a^2 + 2ar + 2r^2) \right) \quad (24.36)$$

or

$$\mathbf{E} = \frac{q}{4\pi\epsilon_0 r^2} \left[ 1 - e^{-2r/a} \left( 1 + \frac{2r}{a} + \frac{2r^2}{a^2} \right) \right] \hat{\mathbf{r}}. \quad (24.37)$$

This electric field is finite (zero) at the origin, and decays to zero at spatial infinity. Much nicer physically, although a lot harder to work with. It’s also not clear we should always consider an electron to be in the ground state of Hydrogen . . .

### 24.3.2 Spectrum

Once an electron is in a stationary state of Hydrogen, it will remain there (*getting it into one* is another issue). If there is some perturbation, and the electron moves from one stationary state to another, then it will do so in a quantized way – i.e. transitions between states occur with jumps in energy related to the difference of integers (squared). For example, if we go from some initial state  $n_i$  (set of states) to a final state  $n_f$ , the energy change is:

$$E_i - E_f = E_1 \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right). \quad (24.38)$$



Suppose the energy is released as radiation. We know, from the Planck formula, that  $E = h\nu$  for a photon, so

$$\nu = \frac{E_1}{h} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right), \quad (24.39)$$

or, in terms of the wavelength of the emitted light  $\lambda = c/\nu$ ,

$$\frac{1}{\lambda} = \frac{E_1}{hc} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = 1.097 \times 10^7 \text{ m}^{-1} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (24.40)$$

where the constant  $R = \frac{m}{4\pi c \hbar^3} \left( \frac{e^2}{4\pi \epsilon_0} \right)^2 = 1.097 \times 10^7 \text{ m}^{-1}$  is the Rydberg constant.

### Homework

Reading: Griffiths, pp. 145–159.

#### Problem 24.1

Griffiths 4.13 (parts a. and b.). Practice calculating expectation values for Hydrogen.

#### Problem 24.2

Griffiths 4.14. Most probable electron radius for the ground state of Hydrogen.

#### Problem 24.3

Griffiths 4.15. States that are not the ground state, and their time dependence. Use (4.89) to write the full functional form of the wave function  $\Psi(r, \theta, \phi, t)$ .