

HYDROGEN ATOM - SERIES SOLUTION AND BOHR ENERGY LEVELS

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Reference: Griffiths, David J. (2005), *Introduction to Quantum Mechanics*, 2nd Edition; Pearson Education - Sec 4.2.1.

Shankar, R. (1994), *Principles of Quantum Mechanics*, Plenum Press. Chapter 13, Exercises 13.1.1 - 13.1.2.

[This page follows the derivation given in Griffiths. The discussion in Shankar's chapter 13 is similar, but he uses Gaussian units, so the answer looks different. However, I can't be bothered going through the whole derivation again with different units, since the steps are essentially the same.]

We saw in an earlier post that the radial part of the three-dimensional Schrödinger equation for the hydrogen atom can be reduced to the differential equation

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

where

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho) \quad (2)$$

$$u(r) \equiv rR(r) \quad (3)$$

$$\rho = \kappa r \quad (4)$$

$$\rho_0 = \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa} \quad (5)$$

$$\kappa = \frac{\sqrt{-2mE}}{\hbar} \quad (6)$$

and $R(r)$ is the radial part of the three-dimensional wave function.

Our task here is to solve 1 by using the same method as for the harmonic oscillator. We propose a solution of the form

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j \quad (7)$$

and attempt to determine the coefficients c_j . The two derivatives needed in the equation are

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1} \quad (8)$$

$$\frac{d^2v}{d\rho^2} = \sum_{j=0}^{\infty} j(j-1) c_j \rho^{j-2} \quad (9)$$

We now plug these back into 1 and fiddle with the summation indexes so that every term in every sum is a multiple of ρ^j .

$$\sum_{j=0}^{\infty} j(j-1) c_j \rho^{j-1} + 2(l+1) \sum_{j=0}^{\infty} j c_j \rho^{j-1} - 2 \sum_{j=0}^{\infty} j c_j \rho^j + (\rho_0 - 2l - 2) \sum_{j=0}^{\infty} c_j \rho^j = 0 \quad (10)$$

The two terms containing ρ^{j-1} can be converted to sums over ρ^j by shifting the summation index from j to $j+1$. This means that the sum becomes

$$\sum_{j=-1}^{\infty} (j+1) j c_{j+1} \rho^j + 2(l+1) \sum_{j=-1}^{\infty} (j+1) c_{j+1} \rho^j - 2 \sum_{j=0}^{\infty} j c_j \rho^j + (\rho_0 - 2l - 2) \sum_{j=0}^{\infty} c_j \rho^j = 0 \quad (11)$$

Note that the term with $j = -1$ in the first two sums is zero because of the $(j+1)$ factor, so we can start the sum at $j = 0$. Since ρ^j is now a common factor in all sums we can write the overall sum as

$$\sum_{j=0}^{\infty} [(j+1) j c_{j+1} + 2(l+1)(j+1) c_{j+1} - 2j c_j + (\rho_0 - 2l - 2) c_j] \rho^j = 0 \quad (12)$$

Because each power series is unique (a mathematical theorem), the only way this sum can be valid for all values of ρ is if all the coefficients are zero. That is

$$(j+1) j c_{j+1} + 2(l+1)(j+1) c_{j+1} - 2j c_j + (\rho_0 - 2l - 2) c_j = 0 \quad (13)$$

This can be rewritten as a recursion relation:

$$c_{j+1} = \frac{2(j+l+1) - \rho_0}{(j+1)(j+2(l+1))} c_j \quad (14)$$

[This equation is essentially the same as Shankar's 13.1.11 if you replace $j \rightarrow k$ and use Gaussian units in ρ_0 .]

The argument at this point is again similar to that for the harmonic oscillator: we examine the behaviour for large j . In that case, we can ignore the $l+1$ and ρ_0 terms and write

$$c_{j+1} \sim \frac{2j}{j(j+1)}c_j \quad (15)$$

$$= \frac{2}{j+1}c_j \quad (16)$$

(We could also ignore the 1 in the denominator, but keeping it makes the argument easier, as we will see.) If we took this as an exact recursion relation, then starting with some initial constant c_0 , we get

$$c_1 = \frac{2}{1}c_0 \quad (17)$$

$$c_2 = \frac{2^2}{2 \times 1}c_0 \quad (18)$$

$$c_3 = \frac{2^3}{3 \times 2 \times 1}c_0 \quad (19)$$

$$c_j = \frac{2^j}{j!}c_0 \quad (20)$$

$$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j \quad (21)$$

$$= c_0 e^{2\rho} \quad (22)$$

In the last line we used the series expansion for the exponential function. Returning for a moment to the original definition of $v(\rho)$, we get

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho) \quad (23)$$

$$= c_0 \rho^{l+1} e^{\rho} \quad (24)$$

Thus the infinite series solution gives a value for u that increases exponentially for large ρ , which isn't normalizable, so isn't a valid solution. The only way to resolve this problem is again the same as in the harmonic oscillator case, which is to require the series to terminate after a finite number of terms. That is, we must have, for some value of j ,

$$2(j+l+1) = \rho_0 \quad (25)$$

That is, ρ_0 must be an even integer, which we can define as $2n$. Recalling the definition of ρ_0 from above, we therefore have the condition which quantizes the energy levels in the hydrogen atom:

$$\rho_0 = \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa} \quad (26)$$

$$= 2n \quad (27)$$

so

$$\kappa = \frac{me^2}{4\pi\epsilon_0\hbar^2n} \quad (28)$$

But $\kappa = \frac{\sqrt{-2mE}}{\hbar}$, so for the energy levels, we get

$$E = -\frac{1}{n^2} \frac{me^4}{2\hbar^2(4\pi\epsilon_0)^2} \quad (29)$$

This is the Bohr formula (although Bohr got the formula without using the Schrödinger equation) for the energy levels of hydrogen. [Again, this is equivalent to Shankar's 13.1.16 if you use Gaussian units, so that the $(4\pi\epsilon_0)^2$ factor becomes 1.]

The degeneracy of each energy level is found by noting that for a given value of n , any value of l is possible such that $j + l + 1 = n$. Since j is just the index on the series coefficient c_j , this means that l can be any value from 0 up to $n - 1$. For each l , the z component of angular momentum can have any value from $m = -l$ up to $m = +l$, which gives $2l + 1$ possibilities for each l . Thus the degeneracy for energy state E_n is

$$d(n) = \sum_{l=0}^{n-1} (2l + 1) \quad (30)$$

$$= 2\frac{1}{2}(n-1)n + n \quad (31)$$

$$= n^2 \quad (32)$$

where we've used the formula

$$\sum_{l=1}^N l = \frac{1}{2}N(N+1) \quad (33)$$

Before leaving the series solution, we need to point out that the polynomials produced by 14, with the constraint that $\rho_0 = 2n$, are known mathematically as the *associated Laguerre polynomials*. They can be written as derivatives. First we define the ordinary Laguerre polynomials L_q :

$$L_q(x) = e^x \frac{d^q}{dx^q} (e^{-x} x^q) \quad (34)$$

Now the associated Laguerre polynomials L_{q-p}^p which depend on two parameters can be defined in terms of the ordinary Laguerre polynomials:

$$L_{q-p}^p(x) = (-1)^p \frac{d^p}{dx^p} (L_q(x)) \quad (35)$$

A more useful formula for the associated Laguerre polynomials is

$$L_n^k(x) = \sum_{j=0}^n \frac{(-1)^j (n+k)!}{(n-j)! (k+j)! j!} x^j \quad (36)$$

In terms of associated Laguerre polynomials, the solution of 1 is (apart from normalization)

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho) \quad (37)$$

We can verify that this is the solution of 1 by direct substitution. First, we plug in the correct indexes into 36:

$$L_{n-l-1}^{2l+1}(2\rho) = \sum_{j=0}^{n-l-1} \frac{(-1)^j 2^j (n+l)!}{(n-l-j-1)! (2l+j+1)! j!} \rho^j \quad (38)$$

Now we define the coefficients in the polynomial and show that the recurrence relation 14 is valid:

$$c_j = \frac{(-1)^j 2^j (n+l)!}{(n-l-j-1)! (2l+j+1)! j!} \quad (39)$$

$$\frac{c_{j+1}}{c_j} = \frac{-2(n-l-1-j)}{(j+1)(2l+j+2)} \quad (40)$$

This is the same recurrence relation provided $\rho_0 = 2n$. However, this isn't enough to verify the solution since other definitions of c_j would give the same relation (for example, we could leave out the $(n+l)!$ factor in the numerator and still get the same recurrence relation). To verify that the polynomials are in fact solutions, we can work out their derivatives and plug them into 1 directly.

We get

$$\sum_{j=0}^{n-l-1} [c_j(j-1)j\rho^{j-1} + 2(l+1-\rho)c_jj\rho^{j-1} + 2(n-l-1)c_j\rho^j] = \quad (41)$$

$$\sum_{j=0}^{n-l-1} [c_j(j-1)j\rho^{j-1} + 2(l+1)c_jj\rho^{j-1} + -2jc_j\rho^j + 2(n-l-1)c_j\rho^j] \quad (42)$$

We can now shift the summation index for the first two terms so that we sum over $j+1$ instead of j . This results in

$$\sum_{j=-1}^{n-l-2} [c_{j+1}j(j+1) + 2(l+1)(j+1)c_{j+1}]\rho^j + \sum_{j=0}^{n-l-1} [-2jc_j + 2(n-l-1)c_j]\rho^j \quad (43)$$

In the first sum, the $j = -1$ term is zero due to the $(j+1)$ factor, so we can start both sums from $j = 0$. Thus for all values of j from 0 to $n-l-2$, we can examine the coefficient of ρ^j :

$$c_{j+1}(j+1)(j+2l+2) + c_j(-2j+2n-2l-2) \quad (44)$$

Using the relation between c_j and c_{j+1} above, we get

$$\frac{c_{j+1}}{c_j}(j+1)(j+2l+2) + (-2j+2n-2l-2) = 2(j+l+1-n) + 2(-j+n-l-1) \quad (45)$$

$$= 0 \quad (46)$$

For the one remaining term in the second sum where $j = n-l-1$ we note that this term is zero on its own, since $(-j+n-l-1) = 0$ in this case. Thus the overall sum satisfies the original differential equation 1.

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