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

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

where

$$\begin{aligned}
u(\rho) &= \rho^{l+1}e^{-\rho}v(\rho) && (2)\\
u(r) &\equiv rR(r) && (3)\\
\rho &= \kappa r && (4)\\
\rho_0 &= \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa} && (5)\\
\kappa &= \frac{\sqrt{-2mE}}{\hbar} && (6)
\end{aligned}$$

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

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

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

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

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} jc_j\rho^{j-1} \tag{8}$$

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

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

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

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

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

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

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

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

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

This can be rewritten as a recursion relation:

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

[This equation is essentially the same as Shankar's 13.1.11 if you replace $j \to k$ 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

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

$$= \frac{2}{j+1}c_j \tag{16}$$

(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

$$c_1 = \frac{2}{1}c_0 \tag{17}$$

$$c_2 = \frac{2^2}{2\times 1}c_0 \tag{18}$$

$$c_3 = \frac{2^3}{3\times 2\times 1}c_0 \tag{19}$$

$$c_j = \frac{2^j}{j!}c_0 \tag{20}$$

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

$$= c_0 e^{2\rho} \tag{22}$$

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

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

$$= c_0\rho^{l+1}e^{\rho} \tag{24}$$

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,

$$2(j+l+1) = \rho_0 \tag{25}$$

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:

$$\rho_0 = \frac{me^2}{2\pi\varepsilon_0\hbar^2\kappa} \tag{26}$$
$$= 2n \tag{27}$$

so

$$\kappa = \frac{me^2}{4\pi\varepsilon_0\hbar^2 n} \tag{28}$$

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

$$E = -\frac{1}{n^2}\frac{me^4}{2\hbar^2(4\pi\varepsilon_0)^2} \tag{29}$$

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 $(4\pi\varepsilon_0)^2$ 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

$$d(n) = \sum_{l=0}^{n-1}(2l+1) \tag{30}$$
$$= 2\frac{1}{2}(n-1)n+n \tag{31}$$
$$= n^2 \tag{32}$$

where we've used the formula

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

Before leaving the series solution, we need to point out that the polynomials produced by **??**, 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:

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

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

$$L^p_{q-p}(x) = (-1)^p \frac{d^p}{dx^p}(L_q(x)) \tag{35}$$

A more useful formula for the associated Laguerre polynomials is

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

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

$$v(\rho) = L^{2l+1}_{n-l-1}(2\rho) \tag{37}$$

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

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

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

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

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

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 **??** directly.

We get

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

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

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

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

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:

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

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

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

$$=0 \tag{46}$$

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 **??**.

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