HYDROGEN ATOM - SERIES SOLUTION AND BOHR ENERGY LEVELS

Link to: physicspages home page.
To leave a comment or report an error, please use the auxiliary blog.
Post date: 7 Jun 2011.

[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

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho) \quad (2)$$
$$u(r) \equiv r R(r) \quad (3)$$
$$\rho = \kappa r \quad (4)$$
$$\rho_0 = \frac{m e^2}{2 \pi \epsilon_0 \hbar^2 \kappa} \quad (5)$$
$$\kappa = \sqrt{-\frac{2mE}{\hbar}} \quad (6)$$

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

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

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

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

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

$$\sum_{j=-1}^{\infty} (j+1) c_{j+1} \rho^j + 2(l+1) \sum_{j=-1}^{\infty} (j+1) c_{j+1} \rho^j - 2 \sum_{j=0}^{\infty} j c_j \rho^j + (\rho_0 - 2l - 2) \sum_{j=0}^{\infty} c_j \rho^j = 0$$  \hspace{1cm} (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 $\rho^j$ is now a common
factor in all sums we can write the overall sum as

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

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

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

This can be rewritten as a recursion relation:

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

[This equation is essentially the same as Shankar’s 13.1.11 if you replace
$j \rightarrow k$ and use Gaussian units in $\rho_0$.]
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 $\rho_0$ terms and write

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

$$= \frac{2}{j+1} c_j$$  \hfill (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

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

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

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

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

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

$$= c_0 e^{2\rho}$$  \hfill (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

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

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

Thus the infinite series solution gives a value for $u$ that increases exponentially for large $\rho$, 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 $j$,

$$2(j + l + 1) = \rho_0$$  \hfill (25)
That is, $\rho_0$ must be an even integer, which we can define as $2n$. Recalling the definition of $\rho_0$ from above, we therefore have the condition which quantizes the energy levels in the hydrogen atom:

\[
\rho_0 = \frac{me^2}{2\pi\varepsilon_0\hbar^2\kappa} = 2n
\]

so

\[
\kappa = \frac{me^2}{4\pi\varepsilon_0\hbar^2 n}
\]

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

\[
E = -\frac{1}{n^2} \frac{me^4}{2\hbar^2(4\pi\varepsilon_0)^2}
\]

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

\[
d(n) = \sum_{l=0}^{n-1} (2l + 1) = \frac{1}{2} (n - 1) n + n
\]

where we’ve used the formula

\[
\sum_{l=1}^{N} l = \frac{1}{2} N (N + 1)
\]
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 $L_q$:

$$L_q(x) = e^x \frac{d^q}{dx^q} (e^{-x} x^q)$$  \hspace{1cm} (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:

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

A more useful formula for the associated Laguerre polynomials is

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

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

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

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

$$L_{n-l-1}^{2l+1}(2\rho) = \sum_{j=0}^{n-l-1} \frac{(-1)^j2^j(n+l)!}{(n-l-j-1)!(2l+j+1)!j!} \rho^j$$  \hspace{1cm} (38)$$

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

$$c_j = \frac{(-1)^j2^j(n+l)!}{(n-l-j-1)!(2l+j+1)!j!} \frac{c_{j+1}}{c_j} = \frac{-2(n-l-1-j)}{(j+1)(2l+j+2)}$$  \hspace{1cm} (39)$$

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

(41)

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

(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

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

(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 \(\rho^j\):

\[ c_{j+1}(j+1)(j+2l+2) + c_j(-2j+2n-2l-2) \]

(44)

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

\[ \frac{c_{j+1}}{c_j}(j+1)(j+2l+2) + (-2j+2n-2l-2) = 2(j+l+1-n) + 2(-j+n-l-1) \]

(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.

**Pingbacks**

Pingback: Hydrogen atom - radial function examples
Pingback: Hydrogen atom - Laguerre polynomials example
Pingback: Hydrogen atom - mean radius of electron position
Pingback: Hydrogen atom - spectrum
Pingback: Earth-Sun system as a quantum atom
Pingback: Momentum space in 3-d
Pingback: Hydrogen atom - complete wave function
Pingback: Hydrogen atom: probability of finding electron inside the nucleus