

## FEYNMAN-HELLMANN THEOREM: HYDROGEN ATOM MEAN VALUES

Link to: physicspages home page.

To leave a comment or report an error, please use the auxiliary blog.

References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 6.33.

As an application of the Feynman-Hellmann theorem, we can derive the expressions for  $\langle \frac{1}{r} \rangle$  and  $\langle \frac{1}{r^2} \rangle$  that we used earlier in the relativistic correction to the hydrogen energy. We start with the radial hamiltonian for hydrogen:

$$(0.1) \quad H = -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

and the Bohr energy levels:

$$(0.2) \quad E = -\frac{1}{n^2} \frac{me^4}{2\hbar^2(4\pi\epsilon_0)^2}$$

In order to do the calculations, we need to express the quantum number  $n$  in terms of the angular momentum quantum number  $\ell$ . Looking back at the derivation of  $n$ , we see that it was defined as  $n = j + \ell + 1$  where  $j$  was an integer that determined when the series obtained in the solution of the radial equation terminated. (Note:  $j$  is *not* the total angular momentum!) We then get

$$(0.3) \quad E = -\frac{1}{(j + \ell + 1)^2} \frac{me^4}{2\hbar^2(4\pi\epsilon_0)^2}$$

To get  $\langle \frac{1}{r} \rangle$  we note that it occurs in the third term of  $H$  and a parameter that occurs in that term alone is  $e$ , so we apply the theorem to that parameter.

$$(0.4) \quad \frac{\partial E}{\partial e} = \langle \psi_n \left| \frac{\partial H}{\partial e} \right| \psi_n \rangle$$

$$(0.5) \quad = -\frac{e}{2\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle$$

$$(0.6) \quad = -\frac{2\hbar^2}{ema} \left\langle \frac{1}{r} \right\rangle$$

where in the last line we expressed the result in terms of the Bohr radius  $a = 4\pi\epsilon_0\hbar^2/me^2$ .

From the energy expression

$$(0.7) \quad \frac{\partial E}{\partial e} = -\frac{1}{(j+l+1)^2} \frac{4me^3}{2\hbar^2(4\pi\epsilon_0)^2}$$

$$(0.8) \quad = -\frac{2\hbar^2}{mea^2(j+l+1)^2}$$

$$(0.9) \quad = -\frac{2\hbar^2}{mea^2n^2}$$

Comparing the two we get

$$(0.10) \quad \left\langle \frac{1}{r} \right\rangle = \frac{1}{an^2}$$

To find  $\left\langle \frac{1}{r^2} \right\rangle$ , we use the second term in  $H$  and choose the parameter to be  $\lambda = \ell$ .

$$(0.11) \quad \frac{\partial E}{\partial \ell} = \langle \psi_n \left| \frac{\partial H}{\partial \ell} \right| \psi_n \rangle$$

$$(0.12) \quad = (2\ell+1) \frac{\hbar^2}{2m} \left\langle \frac{1}{r^2} \right\rangle$$

$$(0.13) \quad = \left( \ell + \frac{1}{2} \right) \frac{\hbar^2}{m} \left\langle \frac{1}{r^2} \right\rangle$$

From the energy expression

$$(0.14) \quad \frac{\partial E}{\partial \ell} = \frac{me^4}{(j + \ell + 1)^3 \hbar^2 (4\pi\epsilon_0)^2}$$

$$(0.15) \quad = \frac{\hbar^2}{mn^3a^2}$$

Comparing the two we get

$$(0.16) \quad \left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(\ell + \frac{1}{2}) a^2 n^3}$$

PINGBACKS

Pingback: Fine structure of hydrogen: relativistic correction