

FEYNMAN-HELLMANN THEOREM: HYDROGEN ATOM MEAN VALUES

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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:

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

and the Bohr energy levels:

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

In order to do the calculations, we need to express the quantum number n in terms of the angular momentum quantum number ℓ . 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

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

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.

$$\frac{\partial E}{\partial e} = \langle \psi_n \left| \frac{\partial H}{\partial e} \right| \psi_n \rangle \quad (4)$$

$$= -\frac{e}{2\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle \quad (5)$$

$$= -\frac{2\hbar^2}{ema} \left\langle \frac{1}{r} \right\rangle \quad (6)$$

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

$$\frac{\partial E}{\partial e} = -\frac{1}{(j+l+1)^2} \frac{4me^3}{2\hbar^2(4\pi\epsilon_0)^2} \quad (7)$$

$$= -\frac{2\hbar^2}{mea^2(j+l+1)^2} \quad (8)$$

$$= -\frac{2\hbar^2}{mea^2n^2} \quad (9)$$

Comparing the two we get

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{an^2} \quad (10)$$

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

$$\frac{\partial E}{\partial \ell} = \langle \psi_n | \frac{\partial H}{\partial \ell} | \psi_n \rangle \quad (11)$$

$$= (2\ell+1) \frac{\hbar^2}{2m} \left\langle \frac{1}{r^2} \right\rangle \quad (12)$$

$$= \left(\ell + \frac{1}{2} \right) \frac{\hbar^2}{m} \left\langle \frac{1}{r^2} \right\rangle \quad (13)$$

From the energy expression

$$\frac{\partial E}{\partial \ell} = \frac{me^4}{(j+l+1)^3 \hbar^2 (4\pi\epsilon_0)^2} \quad (14)$$

$$= \frac{\hbar^2}{mn^3a^2} \quad (15)$$

Comparing the two we get

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{\left(\ell + \frac{1}{2}\right) a^2 n^3} \quad (16)$$

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