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 $\left\langle\frac{1}{r}\right\rangle$ and $\left\langle\frac{1}{r^2}\right\rangle$ that we used earlier in the relativistic correction to the hydrogen energy. We start with the radial hamiltonian for hydrogen:

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

and the Bohr energy levels:

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

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

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

To get $\left\langle\frac{1}{r}\right\rangle$ 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.

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

$$= -\frac{e}{2\pi\varepsilon_0}\left\langle \frac{1}{r} \right\rangle \tag{5}$$

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

where in the last line we expressed the result in terms of the Bohr radius $a = 4\pi\varepsilon_0\hbar^2/me^2$.

From the energy expression

$$\frac{\partial E}{\partial e} = -\frac{1}{(j+\ell+1)^2}\frac{4me^3}{2\hbar^2(4\pi\varepsilon_0)^2} \tag{7}$$

$$= -\frac{2\hbar^2}{mea^2\,(j+\ell+1)^2} \tag{8}$$

$$= -\frac{2\hbar^2}{mea^2n^2} \tag{9}$$

Comparing the two we get

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

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

$$\frac{\partial E}{\partial \ell} = \left\langle \psi_n \left| \frac{\partial H}{\partial \ell} \right| \psi_n \right\rangle \tag{11}$$

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

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

From the energy expression

$$\frac{\partial E}{\partial \ell} = \frac{me^4}{(j+\ell+1)^3\hbar^2(4\pi\varepsilon_0)^2} \tag{14}$$

$$= \frac{\hbar^2}{mn^3a^2} \tag{15}$$

Comparing the two we get

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

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