HYDROGEN ATOM: POWERS OF THE MOMENTUM OPERATOR

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 6.15.

In this post, we'll derive results concerning powers of the momentem operator p when applied to the $l=0$ states of hydrogen. The general form of the hydrogen wave function is

$$\psi_{nlm}(r,\theta,\phi)=R_{nl}(r)Y_l^m(\theta,\phi) \tag{0.1}$$

where R is the radial function and Y_l^m is a spherical harmonic. If $l=0$, then the only possible value of m is $m=0$ and $Y_0^0=1/\sqrt{4\pi}$, which is independent of θ and ϕ. In spherical coordinates, the square of the momentum operator is then

$$p^2=-\hbar^2\nabla^2=-\frac{\hbar^2}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) \tag{0.2}$$

We'd like to show that this operator is hermitian, that is, for two functions $f(r)$ and $g(r)$ that

$$\left\langle f\left|p^2 g\right.\right\rangle=\left\langle p^2 f\left|g\right.\right\rangle \tag{0.3}$$

We start with

$$\begin{aligned}
p^2 g &= -\frac{\hbar^2}{r^2}\frac{d}{dr}\left(r^2\frac{dg}{dr}\right) && (0.4)\\
&= -\frac{\hbar^2}{r^2}\left(2rg'+r^2g''\right) && (0.5)\\
&= -\hbar^2\left(2\frac{g'}{r}+g''\right) && (0.6)
\end{aligned}$$

We then get

$$\left\langle f \left| p^2 g \right. \right\rangle = -4\pi\hbar^2 \int_0^\infty \frac{f}{r^2}\left(2rg' + r^2 g''\right) r^2 dr \tag{0.7}$$

$$= -4\pi\hbar^2 \int_0^\infty f\left(2rg' + r^2 g''\right) dr \tag{0.8}$$

$$= -4\pi\hbar^2 \left[r^2 f g' \Big|_0^\infty - \int_0^\infty r^2 \left(f'g' + fg''\right) dr + \int_0^\infty r^2 f g'' dr \right] \tag{0.9}$$

$$= -4\pi\hbar^2 \left[r^2 f g' \Big|_0^\infty - \int_0^\infty r^2 f' g' dr \right] \tag{0.10}$$

$$= -4\pi\hbar^2 \left[r^2 f g' \Big|_0^\infty - r^2 f' g \Big|_0^\infty + \int_0^\infty \left(2rf' + r^2 f\right) g dr \right] \tag{0.11}$$

$$= -4\pi\hbar^2 \int_0^\infty \left(2rf' + r^2 f\right) g dr \tag{0.12}$$

$$= \left\langle p^2 f \left| g \right. \right\rangle \tag{0.13}$$

where in the second-to-last line we used the fact that all radial functions in the hydrogen atom have an $e^{-r/na}$ term multiplied by a polynomial in r. The exponential ensures the integrated terms are zero at infinity, and the r^2 factor ensures they are zero at $r = 0$. Thus p^2 is hermitian.

For p^4, we start from 0.6 and apply 0.2:

$$p^4 = -\hbar^4 \nabla^2 \left(2\frac{g'}{r} + g''\right) \tag{0.14}$$

For the first term, we have

$$\nabla^2\frac{g'}{r} = \nabla\cdot\left(\nabla\frac{g'}{r}\right) \tag{0.15}$$

$$= \nabla\cdot\left[g'\nabla\frac{1}{r}+\frac{1}{r}\nabla g'\right] \tag{0.16}$$

$$= g'\nabla^2\frac{1}{r}+2\left(\nabla\frac{1}{r}\right)\cdot\left(\nabla g'\right)+\frac{1}{r}\nabla^2 g' \tag{0.17}$$

$$= -4\pi\delta\left(\mathbf{r}\right)g'-\frac{2}{r^2}\hat{\mathbf{r}}\cdot\left(g''\hat{\mathbf{r}}\right)+\frac{1}{r}\nabla^2 g' \tag{0.18}$$

$$= -4\pi\delta\left(\mathbf{r}\right)g'-2\frac{g''}{r^2}+\frac{1}{r^3}\frac{d}{dr}\left(r^2 g''\right) \tag{0.19}$$

$$= -4\pi\delta\left(\mathbf{r}\right)g'-2\frac{g''}{r^2}+2\frac{g''}{r^2}+\frac{g^{(3)}}{r} \tag{0.20}$$

$$= -4\pi\delta\left(\mathbf{r}\right)g'+\frac{g^{(3)}}{r} \tag{0.21}$$

where the notation $g^{(i)}$ denotes the ith derivative and we've used a couple of earlier results to get the fourth line:

$$\nabla^2\frac{1}{r} = -4\pi\delta\left(\mathbf{r}\right) \tag{0.22}$$

$$\nabla\frac{1}{r} = -\frac{\hat{\mathbf{r}}}{r^2} \tag{0.23}$$

For the second term in 0.14 we have

$$\nabla^2 g'' = \frac{1}{r^2}\frac{d}{dr}\left(r^2 g^{(3)}\right) \tag{0.24}$$

$$= 2\frac{g^{(3)}}{r}+g^{(4)} \tag{0.25}$$

Inserting 0.21 and 0.25 into 0.14 we get

$$p^4 g = \hbar^4\left(\frac{4}{r}g^{(3)}+g^{(4)}-8\pi\delta\left(\mathbf{r}\right)g'\right) \tag{0.26}$$

Now we want to calculate $\left\langle f\left|p^4 g\right.\right\rangle$ and compare it with $\left\langle g\left|p^4 f\right.\right\rangle$, so we have

$$\frac{1}{\hbar^4}\left\langle f\left|p^4 g\right.\right\rangle = 4\pi\int_0^\infty\left(4rfg^{(3)}+r^2fg^{(4)}\right)-8\pi\int\delta(\mathbf{r})\,fg'd^3\mathbf{r} \tag{0.27}$$

$$\frac{1}{\hbar^4}\left\langle g\left|p^4 f\right.\right\rangle = 4\pi\int_0^\infty\left(4rgf^{(3)}+r^2gf^{(4)}\right)-8\pi\int\delta(\mathbf{r})\,gf'd^3\mathbf{r} \tag{0.28}$$

The aim is to integrate by parts enough times to eliminate the derivatives of g under the integral. Again, this is tedious, but we can plow onwards, or else just use some software to ease the task. Using Maple's IntegrationTools[Parts] operation, we find (after eliminating all terms evaluated at $r=\infty$ because they contain an $e^{-r/na}$ factor, and those terms containing a factor of r or r^2 evaluated at $r=0$):

$$\int_0^\infty 4rfg^{(3)}dr = 4f(0)\,g'(0)-8f'(0)\,g(0)-\int_0^\infty g\left(12f''+4rf^{(3)}\right)dr \tag{0.29}$$

$$\int_0^\infty r^2fg^{(4)}dr = -2f(0)\,g'(0)+6f'(0)\,g(0)+\int_0^\infty g\left(12f''+8rf^{(3)}+r^2f^{(4)}\right)dr \tag{0.30}$$

Adding these together and adding on the delta function term in 0.27, we get, by comparing the result with 0.28

$$\frac{1}{4\pi\hbar^4}\left\langle f\left|p^4 g\right.\right\rangle = 2f(0)\,g'(0)-2f'(0)\,g(0)+\int_0^\infty g\left(r^2f^{(4)}+4rf^{(3)}\right)dr-8\pi f(0)\,g'(0) \tag{0.31}$$

$$\left\langle f\left|p^4 g\right.\right\rangle = 8\pi\hbar^4\left(f(0)\,g'(0)-f'(0)\,g(0)\right)+\left\langle g\left|p^4 f\right.\right\rangle+8\pi\hbar^4\left(g(0)\,f'(0)-f(0)\,g'(0)\right) \tag{0.32}$$

$$= \left\langle g\left|p^4 f\right.\right\rangle \tag{0.33}$$

Thus p^4 is also hermitian.

[Note that this is the opposite result to that specified in Griffiths's problem 6.15, where he asks us to prove that p^4 is *not* hermitian. However, Griffiths corrects this result in his errata. Thanks to Jack Whaley-Baldwin (see comments below) for pointing this out.]

PINGBACKS

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