HYDROGEN ATOM - POWERS OF THE MOMENTUM OPERATOR

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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

$$\psi_{nlm}(r,\theta,\phi)=R_{nl}(r)\,Y_l^m(\theta,\phi) \tag{1}$$

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

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

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

$$\left\langle f\left|p^2g\right.\right\rangle=\left\langle p^2f\left|g\right.\right\rangle \tag{3}$$

We start with

$$\begin{aligned}
p^2g&=-\frac{\hbar^2}{r^2}\frac{d}{dr}\left(r^2\frac{dg}{dr}\right) && (4)\\
&=-\frac{\hbar^2}{r^2}\left(2rg'+r^2g''\right) && (5)\\
&=-\hbar^2\left(2\frac{g'}{r}+g''\right) && (6)
\end{aligned}$$

We then get

$$\left\langle f\left|p^2 g\right.\right\rangle = -4\pi\hbar^2\int_0^\infty \frac{f}{r^2}\left(2rg'+r^2g''\right)r^2dr \tag{7}$$
$$= -4\pi\hbar^2\int_0^\infty f\left(2rg'+r^2g''\right)dr \tag{8}$$
$$= -4\pi\hbar^2\left[r^2fg'\Big|_0^\infty - \int_0^\infty r^2\left(f'g'+fg''\right)dr + \int_0^\infty r^2fg''dr\right] \tag{9}$$
$$= -4\pi\hbar^2\left[r^2fg'\Big|_0^\infty - \int_0^\infty r^2f'g'dr\right] \tag{10}$$
$$= -4\pi\hbar^2\left[r^2fg'\Big|_0^\infty - r^2f'g\Big|_0^\infty + \int_0^\infty \left(2rf'+r^2f\right)gdr\right] \tag{11}$$
$$= -4\pi\hbar^2\int_0^\infty \left(2rf'+r^2f\right)gdr \tag{12}$$
$$= \left\langle p^2 f\left|g\right.\right\rangle \tag{13}$$

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 6 and apply 2:

$$p^4 = -\hbar^4\nabla^2\left(2\frac{g'}{r}+g''\right) \tag{14}$$

For the first term, we have

$$\nabla^2 \frac{g'}{r} = \nabla \cdot \left(\nabla \frac{g'}{r} \right) \tag{15}$$
$$= \nabla \cdot \left[g' \nabla \frac{1}{r} + \frac{1}{r} \nabla g' \right] \tag{16}$$
$$= g' \nabla^2 \frac{1}{r} + 2 \left(\nabla \frac{1}{r} \right) \cdot \left(\nabla g' \right) + \frac{1}{r} \nabla^2 g' \tag{17}$$
$$= -4\pi\delta(\mathbf{r}) g' - \frac{2}{r^2} \hat{\mathbf{r}} \cdot \left(g'' \hat{\mathbf{r}} \right) + \frac{1}{r} \nabla^2 g' \tag{18}$$
$$= -4\pi\delta(\mathbf{r}) g' - 2\frac{g''}{r^2} + \frac{1}{r^3} \frac{d}{dr} \left(r^2 g'' \right) \tag{19}$$
$$= -4\pi\delta(\mathbf{r}) g' - 2\frac{g''}{r^2} + 2\frac{g''}{r^2} + \frac{g^{(3)}}{r} \tag{20}$$
$$= -4\pi\delta(\mathbf{r}) g' + \frac{g^{(3)}}{r} \tag{21}$$

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

$$\nabla^2 \frac{1}{r} = -4\pi\delta(\mathbf{r}) \tag{22}$$
$$\nabla \frac{1}{r} = -\frac{\hat{\mathbf{r}}}{r^2} \tag{23}$$

For the second term in 14 we have

$$\nabla^2 g'' = \frac{1}{r^2} \frac{d}{dr} \left(r^2 g^{(3)} \right) \tag{24}$$
$$= 2\frac{g^{(3)}}{r} + g^{(4)} \tag{25}$$

Inserting 21 and 25 into 14 we get

$$p^4 g = \hbar^4 \left(\frac{4}{r} g^{(3)} + g^{(4)} - 8\pi\delta(\mathbf{r}) g' \right) \tag{26}$$

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

$$\frac{1}{\hbar^4}\left\langle f\left|p^4 g\right.\right\rangle = 4\pi\int_0^\infty\left(4rfg^{(3)}+r^2fg^{(4)}\right)-8\pi\int\delta\left(\mathbf{r}\right)fg'd^3\mathbf{r} \quad (27)$$

$$\frac{1}{\hbar^4}\left\langle g\left|p^4 f\right.\right\rangle = 4\pi\int_0^\infty\left(4rgf^{(3)}+r^2gf^{(4)}\right)-8\pi\int\delta\left(\mathbf{r}\right)gf'd^3\mathbf{r} \quad (28)$$

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 $r=0$):

$$\int_0^\infty 4rfg^{(3)}dr = 4f\left(0\right)g'\left(0\right)-8f'\left(0\right)g\left(0\right)-\int_0^\infty g\left(12f''+4rf^{(3)}\right)dr \quad (29)$$

$$\int_0^\infty r^2fg^{(4)}dr = -2f\left(0\right)g'\left(0\right)+6f'\left(0\right)g\left(0\right)+\int_0^\infty g\left(12f''+8rf^{(3)}+r^2f^{(4)}\right)dr \quad (30)$$

Adding these together and adding on the delta function term in 27, we get, by comparing the result with 28

$$\frac{1}{4\pi\hbar^4}\left\langle f\left|p^4 g\right.\right\rangle = 2f\left(0\right)g'\left(0\right)-2f'\left(0\right)g\left(0\right)+\int_0^\infty g\left(r^2f^{(4)}+4rf^{(3)}\right)dr-8\pi f\left(0\right)g'\left(0\right) \quad (31)$$

$$\left\langle f\left|p^4 g\right.\right\rangle = 8\pi\hbar^4\left(f\left(0\right)g'\left(0\right)-f'\left(0\right)g\left(0\right)\right)+\left\langle g\left|p^4 f\right.\right\rangle+8\pi\hbar^4\left(g\left(0\right)f'\left(0\right)-f\left(0\right)g'\left(0\right)\right) \quad (32)$$

$$= \left\langle g\left|p^4 f\right.\right\rangle \quad (33)$$

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 for pointing this out.]

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