

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 momentum operator p when applied to the $l = 0$ states of hydrogen. The general form of the hydrogen wave function is

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

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

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

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

$$\langle f | p^2 g \rangle = \langle p^2 f | g \rangle \quad (3)$$

We start with

$$p^2 g = -\frac{\hbar^2}{r^2} \frac{d}{dr} \left(r^2 \frac{dg}{dr} \right) \quad (4)$$

$$= -\frac{\hbar^2}{r^2} (2rg' + r^2 g'') \quad (5)$$

$$= -\hbar^2 \left(2\frac{g'}{r} + g'' \right) \quad (6)$$

We then get

$$\langle f | p^2 g \rangle = -4\pi\hbar^2 \int_0^\infty \frac{f}{r^2} (2rg' + r^2g'') r^2 dr \quad (7)$$

$$= -4\pi\hbar^2 \int_0^\infty f (2rg' + r^2g'') dr \quad (8)$$

$$= -4\pi\hbar^2 \left[r^2 fg' \Big|_0^\infty - \int_0^\infty r^2 (f'g' + fg'') dr + \int_0^\infty r^2 fg'' dr \right] \quad (9)$$

$$= -4\pi\hbar^2 \left[r^2 fg' \Big|_0^\infty - \int_0^\infty r^2 f'g' dr \right] \quad (10)$$

$$= -4\pi\hbar^2 \left[r^2 fg' \Big|_0^\infty - r^2 f'g \Big|_0^\infty + \int_0^\infty (2rf' + r^2f) g dr \right] \quad (11)$$

$$= -4\pi\hbar^2 \int_0^\infty (2rf' + r^2f) g dr \quad (12)$$

$$= \langle p^2 f | g \rangle \quad (13)$$

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:

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

For the first term, we have

$$\nabla^2 \frac{g'}{r} = \nabla \cdot \left(\nabla \frac{g'}{r} \right) \quad (15)$$

$$= \nabla \cdot \left[g' \nabla \frac{1}{r} + \frac{1}{r} \nabla g' \right] \quad (16)$$

$$= g' \nabla^2 \frac{1}{r} + 2 \left(\nabla \frac{1}{r} \right) \cdot (\nabla g') + \frac{1}{r} \nabla^2 g' \quad (17)$$

$$= -4\pi\delta(\mathbf{r})g' - \frac{2}{r^2} \hat{\mathbf{r}} \cdot (g'' \hat{\mathbf{r}}) + \frac{1}{r} \nabla^2 g' \quad (18)$$

$$= -4\pi\delta(\mathbf{r})g' - 2\frac{g''}{r^2} + \frac{1}{r^3} \frac{d}{dr} (r^2 g'') \quad (19)$$

$$= -4\pi\delta(\mathbf{r})g' - 2\frac{g''}{r^2} + 2\frac{g''}{r^2} + \frac{g^{(3)}}{r} \quad (20)$$

$$= -4\pi\delta(\mathbf{r})g' + \frac{g^{(3)}}{r} \quad (21)$$

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

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

$$\nabla \frac{1}{r} = -\frac{\hat{\mathbf{r}}}{r^2} \quad (23)$$

For the second term in 14 we have

$$\nabla^2 g'' = \frac{1}{r^2} \frac{d}{dr} (r^2 g^{(3)}) \quad (24)$$

$$= 2\frac{g^{(3)}}{r} + g^{(4)} \quad (25)$$

Inserting 21 and 25 into 14 we get

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

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

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

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

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 $r = 0$):

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

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

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

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

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

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

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 (see comments below) for pointing this out.]

PINGBACKS

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