KRAMERS'S RELATION FOR AVERAGES OF RADIAL POWERS IN HYDROGEN

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 6.34.

Here we derive Kramers's relation, which is useful for finding the mean of powers of r for hydrogen wave functions. We begin with the radial equation for hydrogen:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+\left(-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right)u=Eu \tag{1}$$

where $u\equiv rR(r)$ and R is the radial part of the wave function. Note that for a function $f(r)$ the mean is given by

$$\langle f\rangle=\int_0^\infty R(r)f(r)r^2dr=\int_0^\infty u^2f(r)\,dr \tag{2}$$

The Bohr energy is

$$E_n=-\frac{\hbar^2}{2ma^2n^2} \tag{3}$$

with the Bohr radius

$$a=\frac{4\pi\epsilon_0\hbar^2}{me^2} \tag{4}$$

So we can write this as

$$u''=\left(\frac{l(l+1)}{r^2}-\frac{2}{ar}+\frac{1}{a^2n^2}\right)u \tag{5}$$

We can now consider the integral (using 2)

$$\int ur^su''dr=l(l+1)\left\langle r^{s-2}\right\rangle-\frac{2}{a}\left\langle r^{s-1}\right\rangle+\frac{1}{a^2n^2}\left\langle r^s\right\rangle \tag{6}$$

Integrating the integral on the left by parts and as usual discarding the boundary terms which go to zero because u contains a negative exponential which goes to zero at ∞ and a power of r which goes to zero at $r=0$, we get

$$\int ur^{s}u''dr=-\int u'r^{s}u'dr-s\int u'r^{s-1}udr \tag{7}$$

Integrating the second term on the RHS by parts again, we get

$$\int u'r^{s-1}udr=-\int ur^{s-1}u'dr-(s-1)\int u^{2}r^{s-2}dr \tag{8}$$

$$2\int ur^{s-1}u'dr=-(s-1)\int u^{2}r^{s-2}dr \tag{9}$$

$$\int ur^{s-1}u'dr=-\frac{s-1}{2}\left\langle r^{s-2}\right\rangle \tag{10}$$

We can write the last line (by replacing the dummy parameter s by $s+1$):

$$\int ur^{s}u'dr=-\frac{s}{2}\left\langle r^{s-1}\right\rangle \tag{11}$$

Returning to the first term on the RHS of 7, we integrate by parts:

$$\int u'r^{s}u'dr=-2\int\frac{r^{s+1}}{s+1}u'u''dr \tag{12}$$

We can now substitute 5 into the RHS and use 11:

$$\int u'r^{s}u'dr=-2\int\frac{r^{s+1}}{s+1}u'\left(\frac{l(l+1)}{r^{2}}-\frac{2}{ar}+\frac{1}{a^{2}n^{2}}\right)udr \tag{13}$$

$$=-\frac{2}{s+1}\left(-\frac{l(l+1)(s-1)}{2}\left\langle r^{s-2}\right\rangle+\frac{s}{a}\left\langle r^{s-1}\right\rangle-\frac{s+1}{2a^{2}n^{2}}\left\langle r^{s}\right\rangle\right) \tag{14}$$

We can now substitute this result and 11 back into 7:

$$\int ur^{s}u''dr=\frac{2}{s+1}\left(-\frac{l(l+1)(s-1)}{2}\left\langle r^{s-2}\right\rangle+\frac{s}{a}\left\langle r^{s-1}\right\rangle-\frac{s+1}{2a^{2}n^{2}}\left\langle r^{s}\right\rangle\right)+s\frac{s-1}{2}\left\langle r^{s-2}\right\rangle \tag{15}$$

By equating the RHS of this with the RHS of 6 we get, after sorting out terms:

$$\frac{s+1}{n^{2}}\left\langle r^{s}\right\rangle-(2s+1)a\left\langle r^{s-1}\right\rangle+\frac{s}{4}\left[(2l+1)^{2}-s^{2}\right]a^{2}\left\langle r^{s-2}\right\rangle=0 \tag{16}$$

This is Kramers's relation.

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