

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:

$$(0.1) \quad -\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left(-\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right) u = Eu$$

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

$$(0.2) \quad \langle f \rangle = \int_0^\infty R(r) f(r) r^2 dr = \int_0^\infty u^2 f(r) dr$$

The Bohr energy is

$$(0.3) \quad E_n = -\frac{\hbar^2}{2ma^2n^2}$$

with the Bohr radius

$$(0.4) \quad a = \frac{4\pi\epsilon_0\hbar^2}{me^2}$$

So we can write this as

$$(0.5) \quad u'' = \left(\frac{l(l+1)}{r^2} - \frac{2}{ar} + \frac{1}{a^2n^2} \right) u$$

We can now consider the integral (using 0.2)

$$(0.6) \quad \int ur^s u'' dr = l(l+1) \langle r^{s-2} \rangle - \frac{2}{a} \langle r^{s-1} \rangle + \frac{1}{a^2n^2} \langle r^s \rangle$$

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

$$(0.7) \quad \int ur^s u'' dr = - \int u' r^s u' dr - s \int u' r^{s-1} u dr$$

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

$$(0.8) \quad \int u' r^{s-1} u dr = - \int ur^{s-1} u' dr - (s-1) \int u^2 r^{s-2} dr$$

$$(0.9) \quad 2 \int ur^{s-1} u' dr = - (s-1) \int u^2 r^{s-2} dr$$

$$(0.10) \quad \int ur^{s-1} u' dr = - \frac{s-1}{2} \langle r^{s-2} \rangle$$

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

$$(0.11) \quad \int ur^s u' dr = - \frac{s}{2} \langle r^{s-1} \rangle$$

Returning to the first term on the RHS of 0.7, we integrate by parts:

$$(0.12) \quad \int u' r^s u' dr = -2 \int \frac{r^{s+1}}{s+1} u' u'' dr$$

We can now substitute 0.5 into the RHS and use 0.11:

$$(0.13) \quad \int u' r^s u' dr = -2 \int \frac{r^{s+1}}{s+1} u' \left(\frac{l(l+1)}{r^2} - \frac{2}{ar} + \frac{1}{a^2 n^2} \right) u dr$$

$$(0.14) \quad = - \frac{2}{s+1} \left(- \frac{l(l+1)(s-1)}{2} \langle r^{s-2} \rangle + \frac{s}{a} \langle r^{s-1} \rangle - \frac{s+1}{2a^2 n^2} \langle r^s \rangle \right)$$

We can now substitute this result and 0.11 back into 0.7:

$$(0.15) \quad \int ur^s u'' dr = \frac{2}{s+1} \left(- \frac{l(l+1)(s-1)}{2} \langle r^{s-2} \rangle + \frac{s}{a} \langle r^{s-1} \rangle - \frac{s+1}{2a^2 n^2} \langle r^s \rangle \right) + s \frac{s-1}{2} \langle r^{s-2} \rangle$$

By equating the RHS of this with the RHS of 0.6 we get, after sorting out terms:

$$(0.16) \quad \frac{s+1}{n^2} \langle r^s \rangle - (2s+1) a \langle r^{s-1} \rangle + \frac{s}{4} \left[(2l+1)^2 - s^2 \right] a^2 \langle r^{s-2} \rangle = 0$$

This is Kramers's relation.

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