

KRAMERS'S RELATION FOR AVERAGES OF RADIAL POWERS IN HYDROGEN

Link to: physicspages home page.

To leave a comment or report an error, please use the auxiliary blog and include the title or URL of this post in your comment.

Post date: 26 September 2021.

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:

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

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

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

The Bohr energy is

$$E_n = -\frac{\hbar^2}{2ma^2n^2} \quad (3)$$

with the Bohr radius

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

So we can write this as

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

We can now consider the integral (using 2)

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

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

$$\int ur^s u'' dr = - \int u' r^s u' dr - s \int u' r^{s-1} u dr \quad (7)$$

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

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

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

$$\int ur^{s-1} u' dr = -\frac{s-1}{2} \langle r^{s-2} \rangle \quad (10)$$

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

$$\int ur^s u' dr = -\frac{s}{2} \langle r^{s-1} \rangle \quad (11)$$

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

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

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

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

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

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

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

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

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

This is Kramers's relation.

COMMENTS

From LDG, 7 Jul 2020 18:59

The proof does not cover the case of $s = -1$, since equation 12 cannot be applied.

PINGBACKS

Pingback: Kramers's relation - application to hydrogen mean values