

KRAMERS'S RELATION - APPLICATION TO HYDROGEN MEAN VALUES

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Here are a few examples of using Kramers's relation to calculate means of powers of r for the hydrogen atom. Kramers's relation is

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

If we start with $s = 0$ we get immediately:

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{an^2} \quad (2)$$

From here we can generate increasing powers of r . With $s = 1$

$$\frac{2}{n^2} \langle r \rangle - 3a + \frac{1}{4} [(2l+1)^2 - 1] a^2 \langle r^{-1} \rangle = 0 \quad (3)$$

$$\langle r \rangle = \frac{n^2}{2} \left[3a - \frac{a}{4n^2} [(2l+1)^2 - 1] \right] \quad (4)$$

$$= \frac{a}{2} (3n^2 - l(l+1)) \quad (5)$$

With $s = 2$

$$\frac{3}{n^2} \langle r^2 \rangle - 5a \langle r \rangle + \frac{a^2}{2} [(2l+1)^2 - 4] = 0 \quad (6)$$

Rearranging and substituting for $\langle r \rangle$, we get

$$\langle r^2 \rangle = \frac{n^2}{3} \left(\frac{5a^2}{2} (3n^2 - l(l+1)) - \frac{a^2}{2} [(2l+1)^2 - 4] \right) \quad (7)$$

$$= \frac{a^2 n^2}{2} (5n^2 - 3l(l+1) + 1) \quad (8)$$

With $s = 3$

$$\frac{4}{n^2} \langle r^3 \rangle - 7a \langle r^2 \rangle + \frac{3}{4} \left[(2l+1)^2 - 9 \right] a^2 \langle r \rangle = 0 \quad (9)$$

Substituting for $\langle r \rangle$ and $\langle r^2 \rangle$ we get

$$\langle r^3 \rangle = \frac{n^2}{4} \left(\frac{7a^3 n^2}{2} (5n^2 - 3l(l+1) + 1) - \frac{3a^3}{8} (3n^2 - l(l+1)) \left[(2l+1)^2 - 9 \right] \right) \quad (10)$$

$$= \frac{n^2 a^3}{8} \left[35n^4 + 25n^2 - 30n^2 l(l+1) + l(l+1)(3l(l+1) - 6) \right] \quad (11)$$

If we try to head in the other direction to get values for negative powers of r , we need an extra bit of information to get started. Trying $s = -1$ we have

$$a \langle r^{-2} \rangle - \frac{1}{4} \left[(2l+1)^2 - 1 \right] a^2 \langle r^{-3} \rangle = 0 \quad (12)$$

so we need one of $\langle r^{-2} \rangle$ or $\langle r^{-3} \rangle$ to get the other one. Fortunately, we got $\langle r^{-2} \rangle$ from the Feynman-Hellmann theorem earlier:

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{\left(l + \frac{1}{2}\right) a^2 n^3} \quad (13)$$

Thus we get

$$\langle r^{-3} \rangle = \frac{4}{\left(l + \frac{1}{2}\right) a n^3} \frac{1}{\left[(2l+1)^2 - 1 \right] a^2} \quad (14)$$

$$= \frac{1}{\left(l + \frac{1}{2}\right) l(l+1) n^3 a^3} \quad (15)$$

This provides the formula we used in discussing spin-orbit coupling earlier.

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