Quantum Mechanics 2

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Hydrogen Atom

position expectation values

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Kramers' Relation for $s = 0$

Because the Kramers' relation is a recursion relation,

$$\frac{s+1}{n^2}Z^2\langle r^s\rangle - (2s+1)Za_0\langle r^{s-1}\rangle + \frac{s}{4}[(2l+1)^2 - s^2]a_0^2\langle r^{s-2}\rangle = 0$$

It is a useful expression for finding expectation values of powers of orbital radius only for we know a few of this to begin with.

Let us now consider Kramers' relation with $s = 0$

$$\frac{1}{n^2}Z^2\langle r^0\rangle - Za_0\langle r^{-1}\rangle = 0$$

Since $r^0 = 1$, we have

$$\langle r^{-1}\rangle = \frac{Z}{n^2 a_0}$$

Bohr Radius

The atomic number Z was included here as a placeholder. For Hydrogen, $Z = 1$. In its ground state, $n = 1$,

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{a_0}$$

The Bohr radius is therefore not the average distance of the electron from the nucleus when the atom is in the ground state. Rather, it is the electron distance that renders the energy in its classical form

$$E_n = -\frac{m}{2n^2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{2n^2 a_0} = \left\langle -\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 r} \right\rangle$$

Kramers' Relation for $s = 1$

For $s = 1$, the Kramers' relation is

$$\frac{2}{n^2} Z^2 \langle r^1 \rangle - 3Za_0 \langle r^0 \rangle + \frac{1}{4}[(2l+1)^2 - 1] a_0^2 \langle r^{-1} \rangle = 0$$

Since we have already evaluated $\langle r^{-1} \rangle$, we can use this relation to evaluate the average orbital distance $\langle r \rangle$.

$$\frac{2}{n^2} Z^2 \langle r \rangle = 3Za_0 - \frac{1}{4}[4l^2 + 4l + 1 - 1] a_0^2 \langle r^{-1} \rangle = 3Za_0 - l(l+1) a_0^2 \frac{Z}{n^2 a_0}$$

Thus,

$$\langle r \rangle = \frac{3n^2 - l(l+1)}{2Z} a_0$$

Note that for hydrogen atom in its ground state, $Z = 1, n = 1, l = 0$,

$$\langle r \rangle = \frac{3}{2} a_0$$

The average orbital distance of the electron is 1.5 times the Bohr radius.

Higher s

For $s = 2$, the Kramers' relation is

$$\frac{3}{n^2} Z^2 \langle r^2 \rangle - 5 Z a_0 \langle r^1 \rangle + \frac{2}{4} [(2l+1)^2 - 4] a_0^2 \langle r^0 \rangle = 0$$

This gives us an expression for $\langle r^2 \rangle$.

For $s = 3$, the Kramers' relation yields an expression relating $\langle r^3 \rangle, \langle r^2 \rangle, \langle r^1 \rangle$, so we can use this to find $\langle r^3 \rangle$.

We can therefore find the expectation values of higher positive powers of the distance through successive application of Kramers' relation for higher and higher s.

Negative Powers

We are however not as lucky for negative powers. For $s = -1$, the Kramers' relation is

$$Za_0\langle r^{-2}\rangle - \frac{1}{4}[(2l+1)^2 - 1]a_0^2\langle r^{-3}\rangle = 0$$

We have a dilemma here. While we now have a relationship between $\langle r^{-2}\rangle$ and $\langle r^{-3}\rangle$, at this point, we do not know either of them.

Another method is needed in order to find the starter term $\langle r^{-2}\rangle$.