267(4): Expectation Values of r in the Schrodinger / x Theory

The Schrodinger equation is based on the classical equation:

$$H = E = \frac{p^2}{2m} - \frac{k}{r} \quad -(1)$$

whose solution is the ellipse of x theory:

$$r = \frac{\alpha}{1 + \epsilon \cos\theta} \quad -(2)$$

The Schrodinger equation is obtained from eq. (1) using

$$\underline{p}\,\phi = -i\hbar\,\underline{\nabla}\phi \quad -(3)$$

where ϕ is the wavefunction. So:

$$-\frac{\hbar^2}{2m}\nabla^2\phi = \left(\frac{k}{r} + E\right)\phi \quad -(4)$$

The expectation values of r are:

$$\langle r \rangle = \int \phi^* \frac{\alpha}{1+\epsilon\cos\theta}\,\phi\, d\tau \quad -(5)$$

In the Bohr theory of the atom:

$$\langle r \rangle = \int \phi^* r_B \phi\, d\tau \quad -(6)$$

$$= r_B \int \phi^* \phi\, d\tau$$

2) The Born normalization is:

$$\int \phi^* \phi \, d\tau = 1 \quad -(7)$$

so

$$\boxed{\langle r \rangle = r_B} \quad -(8)$$

The Bohr theory corresponds to:

$$\alpha = r_B, \quad \epsilon = 0. \quad -(9)$$

The wave functions of the H atom are:

$$\phi = R_{nl}(r) Y_{lm_l}(\phi, \theta) \quad -(10)$$

where $R_{nl}(r)$ are defined in note 267(3) and where the spherical harmonics are defined as follows. The coordinate system is defined in note 267(3) as in VAPS, page 1047.

<u>The Spherical Harmonics</u>

l	m_l	$Y_{lm_l}(\phi, \theta)$
0	0	$\frac{1}{2\pi^{1/2}}$
1	0	$\frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2} \cos\phi$

3)

l	m_l	$Y_{lm_l}(\phi, \theta)$
1	± 1	$\mp \frac{1}{2}\left(\frac{3}{2\pi}\right)^{1/2} \sin\phi \, e^{\pm i\theta}$
2	0	$\frac{1}{4}\left(\frac{5}{\pi}\right)^{1/2}(3\cos^2\phi - 1)$
2	± 1	$\mp \frac{1}{2}\left(\frac{15}{2\pi}\right)^{1/2} \cos\phi \sin\phi \, e^{\pm i\theta}$
2	± 2	$\frac{1}{4}\left(\frac{15}{2\pi}\right)^{1/2} \sin^2\phi \, e^{\pm 2i\theta}$
3	0	$\frac{1}{4}\left(\frac{7}{\pi}\right)^{1/2}(2 - 5\sin^2\phi)\cos\phi$
	± 1	$\mp \frac{1}{8}\left(\frac{21}{\pi}\right)^{1/2}(5\cos^2\phi - 1)\sin\phi \, e^{\pm i\theta}$
	± 2	$\frac{1}{4}\left(\frac{105}{2\pi}\right)^{1/2} \cos\phi \sin^2\phi \, e^{\pm 2i\theta}$
	± 3	$\mp \frac{1}{3}\left(\frac{35}{\pi}\right)^{1/2} \sin^3\phi \, e^{\pm 3i\theta}$

The integral of a function f over $d\tau$ is defined by:

$$\int f \, d\tau = \int_{\theta=0}^{2\pi} \int_{\phi=0}^{\pi} \int_0^{\infty} f r^2 \sin\phi \, dr \, d\phi \, d\theta \quad -(11)$$

4) The required definite integrals are:

$$\int_0^\infty r^n e^{-ar} \, dr = \frac{n!}{a^{n+1}} \quad -(12)$$

and

$$\int_0^\pi \cos^n \phi \sin \phi \, d\phi = \frac{1 + (-1)^n}{n+1} . \quad -(13)$$

<u>Calculation for $n=1, l=0, m_l=0$</u>

This is the 1S orbital of atomic hydrogen, for which:

$$\psi = R_{10} Y_{00} = 2 \left(\frac{1}{r_B} \right)^{3/2} e^{-r/r_B} \cdot \frac{1}{2\pi^{1/2}} \quad -(14)$$

Therefore:

$$\langle r \rangle = \frac{1}{\pi r_B^3} \int_0^{2\pi} r_B \, d\theta \int_0^\pi \sin\phi \, d\phi \int_0^\infty r^2 e^{r/r_B} \, dr \quad -(15)$$

$$= \frac{4}{r_B^2} \int_0^\infty r^2 \exp\left(-\frac{2r}{r_B} \right) dr$$

$$= \frac{4}{r_B^2} \cdot 2! \frac{1}{\left(\frac{2}{r_B} \right)^3}$$

$$= r_B \quad \text{Q.E.D.}$$

5) The expectation value of the radius r in the 1S orbital is the Bohr radius r_B. This well known result is obtained from x theory by use of eq. (9), by assuming that the ellipse becomes a circle whose half right latitude is the Bohr radius.

If this assumption is not made then:

$$\langle r \rangle = \int \psi^* \frac{r_B}{1+\epsilon\cos\theta} \psi \, d\tau \quad - (16)$$

$$= \frac{1}{\pi r_B^2} \int_0^{2\pi} \frac{d\theta}{1+\epsilon\cos\theta} \int_0^{\pi} \sin\phi \, d\phi \int_0^{\infty} r^2 \exp\left(-\frac{2r}{r_B}\right) dr$$

$$= \frac{r_B}{2\pi} \int_0^{2\pi} \frac{d\theta}{1+\epsilon\cos\theta}$$

$$= \frac{r_B}{(1-\epsilon^2)^{1/2}}$$

Therefore the expectation value $\langle r \rangle$ becomes different from the Bohr radius if the Bohr theory is not used.

These calculations can be repeated for

b) different Schroedinger orbitals:

$$n = 1, 2, 3, 4, \ldots$$
$$l = 0, 1, 2, 3, \ldots n-1 \qquad -(17)$$
$$m_l = -l, \ldots, l$$

and this requires the use of computer algebra.

The classical result is eq. (2) in general, and in general, the eccentricity is not zero from eq. (1). The eccentricity is defined by:

$$\epsilon = \left(1 + \frac{2EL^2}{mk^2}\right)^{1/2} \qquad -(18)$$

where

$$k = \frac{e^2}{4\pi\epsilon_0} \qquad -(19)$$

From eqs (16) and (18):

$$\langle r \rangle = \underline{\quad\quad} - r_B \left(\frac{mk^2}{2EL^2}\right) \qquad -(20)$$

It will be interesting to find the properties of $\langle r \rangle$ for higher orbitals

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