Engel 9.14

Problem. Using the 100 or *1s* wave functions provided in Engel, calculate the mean value of the "radius" (the distance of the electron from the nucleus) in H, He^{+}, Li^{2+} and Be^{3+}

Answer. The mean value of *r* is the expectation value of *r*.

The 100 function depends only on *r*, but integration must still be performed with respect to all three spherical polar coordinates because the integrals over θ and ϕ do not equal one, i.e., their values affect the mean value of the radius. Remember that the radial integral will contain an extra factor of *r* because we are trying to establish the expectation value of this quantity.

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In[26]:= Clear[ψ1s, N1s, R1s, a0, Z]
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$$N1s = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a0}\right)^{3/2}$$

$$R1s = e^{-(Z\, r)/a0}$$

$$\psi 1s = N1s\, R1s$$

Out[27]= $\frac{\left(\frac{Z}{a0}\right)^{3/2}}{\sqrt{\pi}}$

Out[28]= $e^{-\frac{r\,Z}{a0}}$

Out[29]= $\frac{e^{-\frac{r\,Z}{a0}} \left(\frac{Z}{a0}\right)^{3/2}}{\sqrt{\pi}}$

The wave function is independent of ϕ, so we will do this integration first

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In[32]:= Clear[ϕint, θint]
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$$\phi int = \int_0^{2\pi} d\phi$$

Out[33]= 2π

The wave function is also independent of θ, so we will do this integration next (and we remember to use sin θ dθ as the index of integration)

In[34]:= $\theta int = \int_0^{\pi} \mathrm{Sin}[\theta]\, d\theta$

Out[34]= 2

The integration with respect to *r* must also include an extra factor of *r* because this is the operator whose expectation value we want to determine, and $r^2\, dr$ as the index of integration. *Z* is the atomic number of each atom.

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In[35]:= Clear[Rint]
         Z = {1, 2, 3, 4}
         Rint = ∫_0^∞ R1s^2 (r) (r^2) ⅆr
         Rint = Simplify[Rint, a0 > 0]

Out[36]= {1, 2, 3, 4}
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Out[37]= $\{\text{If}[\text{Re}[a0] > 0, \frac{3\,a0^4}{8}, \text{Integrate}[e^{-\frac{2r}{a0}} r^3, \{r, 0, \infty\}, \text{Assumptions} \to \text{Re}[a0] \le 0]],$
$\text{If}[\text{Re}[a0] > 0, \frac{3\,a0^4}{128}, \text{Integrate}[e^{-\frac{4r}{a0}} r^3, \{r, 0, \infty\}, \text{Assumptions} \to \text{Re}[a0] \le 0]],$
$\text{If}[\text{Re}[a0] > 0, \frac{a0^4}{216}, \text{Integrate}[e^{-\frac{6r}{a0}} r^3, \{r, 0, \infty\}, \text{Assumptions} \to \text{Re}[a0] \le 0]],$
$\text{If}[\text{Re}[a0] > 0, \frac{3\,a0^4}{2048}, \text{Integrate}[e^{-\frac{8r}{a0}} r^3, \{r, 0, \infty\}, \text{Assumptions} \to \text{Re}[a0] \le 0]]\}$

Out[38]= $\{\frac{3\,a0^4}{8}, \frac{3\,a0^4}{128}, \frac{a0^4}{216}, \frac{3\,a0^4}{2048}\}$

a_0 is the Bohr radius and is a positive real quantity, so this fact can be used to obtain the necessary integral. Now we combine the normalization constant and the three integrals ...

In[39]:= **$N1s^2$ ϕint θint Rint**

Out[39]= $\{\frac{3\,a0}{2}, \frac{3\,a0}{4}, \frac{a0}{2}, \frac{3\,a0}{8}\}$

The Bohr radius is the *most probable* radius of an electron in H, but the mean radius is longer than the Bohr radius (this is to be expected because of the highly unsymmetric nature of the radial distribution function). It is interesting, but not surprising, that the mean radius shrinks as the nucleus becomes more positively charged. The mean radius varies from 1.5 Bohr radii for H, to 0.75 radii for He cation, 0.5 radii for Li dication, and 0.375 radii for Be trication. In fact, the mean radius is inversely related to Z such that $\langle r \rangle Z = 1.5 a_0$.