85(11a): Vacuum Shift for 2s Orbital in H

The 2s orbital in H is:

$$\phi_0(2s) = \frac{1}{2\sqrt{2}\,a^{3/2}}\left(2-\frac{r}{a}\right)e^{-r/(2a)} \quad -(1)$$

so:

$$\nabla^2\phi_0 = \frac{\partial^2\phi_0}{\partial r^2} + \frac{2}{r}\frac{\partial\phi_0}{\partial r} \quad -(2)$$

We have:

$$\phi_0(2s) = \frac{1}{\sqrt{2}\,a^{3/2}}\left(e^{-r/(2a)} - \frac{r}{2a}e^{-r/(2a)}\right) \quad -(3)$$

$$\frac{\partial\phi_0(2s)}{\partial r} = \frac{1}{\sqrt{2}\,a^{3/2}}\left(-\frac{1}{2a}e^{-r/2a} - \frac{1}{2a}e^{-r/(2a)} + \frac{r}{4a^2}e^{-r/(2a)}\right)$$

$$= -\frac{e^{-r/(2a)}}{\sqrt{2}\,a^{5/2}}\left(1-\frac{r}{4a}\right) \quad -(4)$$

and

$$\frac{\partial^2\phi_0(2s)}{\partial r^2} = \frac{e^{-r/(2a)}}{2\sqrt{2}\,a^{7/2}}\left(1-\frac{r}{4a}\right) + \frac{e^{-r/(2a)}}{4\sqrt{2}\,a^{7/2}}$$

$$= \frac{3e^{-r/(2a)}}{4\sqrt{2}\,a^{7/2}}\left(1-\frac{r}{6a}\right) \quad -(5)$$

So:

$$\nabla^2\phi_0 = \frac{3e^{-r/(2a)}}{4\sqrt{2}\,a^{7/2}}\left(1-\frac{r}{6a}\right) - \frac{2e^{-r/(2a)}}{\sqrt{2}\,r\,a^{5/2}}\left(1-\frac{r}{4a}\right)$$

$$= -\frac{4mc}{\hbar}\,\frac{1}{r}\,\frac{1}{2\sqrt{2}\,a^{3/2}}\left(2-\frac{r}{a}\right)e^{-r/(2a)}$$

2)

i.e.

$$\frac{3}{4a^2}\left(1-\frac{r}{6a}\right)-\frac{2}{ar}\left(1-\frac{r}{4a}\right)=-\frac{2mc}{\hbar}\cdot\frac{1}{r_{vac}}\left(2-\frac{r}{a}\right)$$

so:

$$\boxed{\frac{1}{r_{vac}}(2s)=\frac{\hbar}{2mca}\left(\frac{2}{r}-\frac{5}{4a}+\frac{r}{8a^2}\right)\Big/\left(2-\frac{r}{a}\right)} \quad -(7)$$

$-(8)$

Compare this with:

$$\boxed{\frac{1}{r_{vac}}(1s)=\frac{\hbar}{2mca}\left(\frac{2}{r}-\frac{1}{a}\right)} \quad -(9)$$

It can be seen that the vacuum effect on the 2s orbital is different from that on the 1s orbital

Maximum of the 2s Radial Distribution Function

We have seen that the maximum of the 1s radial distribution function is at:

$$r_{max}=a. \quad -(10)$$

At this point:

$$\boxed{\frac{1}{r_{vac}}(1s)\rightarrow+\frac{0.2880}{r}} \quad -(11)$$

meaning that the Coulomb potential becomes less negative ... i.e. ...

The 2s radial distribution function is:

$$f(r)(2s) = 4\pi r^2 \psi(2s)$$

$$= \frac{4\pi}{\sqrt{2}\, a^{3/2}} \left(r^2 - \frac{r^3}{2a} \right) e^{-r/(2a)} \quad -(12)$$

Maxima minima and inflections are given by:

$$\frac{\partial f(r)}{\partial r} = 0 \quad -(13)$$

i.e by $\left(\frac{r}{a}\right)^2 - 8\left(\frac{r}{a}\right) + 8 = 0 \quad -(14)$

or

$$\left.\begin{aligned} r &= 6.8284\, a \text{ and} \\ r &= 1.1716\, a \end{aligned}\right\} -(15)$$

The maximum is taken to be:

$$r_{max} = 6.8284\, a \quad -(16)$$

because we know that it must be much further away from the nucleus than the 1s maximum. Using the value (16) in eq. (8):

$$\boxed{\frac{1}{r_{vac}}(2s) = + \frac{0.02107}{r}} \quad -(17)$$

Comparing eqns. (17) and (11) it is seen that the increase in energy is <u>much less</u> for 2s than 1s, about ten times smaller.