HW #5 Answers.

1. In atomic units

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}-\frac{1}{r}\frac{d}{dr}+\frac{\ell(\ell+1)}{2r^2}\right]\psi = E\psi \quad \text{inside the box}$$

If $\psi = \dfrac{\sin(kr)}{r}$

$$\psi' = \frac{k\cos(kr)}{r} - \frac{\sin(kr)}{r^2}$$

$$\psi'' = -\frac{k^2\sin(kr)}{r} - \frac{2k\cos(kr)}{r^2} + \frac{2\sin(kr)}{r^3}$$

Substitute into the SE

$$\frac{k^2\sin(kr)}{2r} + \frac{k\cos(kr)}{r^2} - \frac{\sin(kr)}{r^3} - \frac{k\cos(kr)}{r^2} + \frac{\sin(kr)}{r}$$

$$+\frac{\ell(\ell+1)}{2r^2}\frac{\sin(kr)}{r} = E\frac{\sin(kr)}{r}$$

The solution is $\ell = 0$, $E = \dfrac{k^2}{2}$

We require $\frac{\sin(kr)}{r} = 0$ at $r = r_0$

$\Rightarrow kr_0 = n\pi$, $k = \frac{n\pi}{r_0}$

So $E = \frac{n^2\pi^2}{2r_0^2}$

undo atomic units

$$E = \frac{n^2\pi^2\hbar^2}{2mr_0^2}$$

2. $E_{1s} = -\frac{1}{2}$ a.u

$V = -\frac{1}{r}$

So the classical turning point is $r = 2$ a.u.

$\psi_{1s} = \frac{1}{\sqrt{\pi}} e^{-r}$

Probability of being inside the classically allowed region is

$$\frac{4\pi}{\pi}\int_0^2 r^2 e^{-2r}\,dr = 4\left[\frac{1}{4} - \frac{13}{4e^4}\right] = 4\,(.1905)$$

$= 0.7620$

So the probability of being in the classically forbidden area is 0.238 (i.e., 23.8%).

two noninteracting ~~He~~ electrons in He

$E_{1s} = -\frac{Z^2}{2}$ (for energy in a.u.)

So $E = -2\left(\frac{4}{2}\right) = -4$ au $\rightarrow -108.84$ eV

$\psi_{NI} = \frac{2^{3/2}}{\sqrt{\pi}} e^{-2r_1} \frac{2^{3/2}}{\sqrt{\pi}} e^{-2r_2} = \frac{2^3}{\pi} e^{-2r_1} e^{-2r_2}$

Now suppose that the electrons interact via a $\delta(r_1 - r_2)$ potential

$$\langle \psi_{NI} | V | \psi_{NI} \rangle = \left(\frac{2^3}{\pi}\right)^2 \int_0^\infty\int_0^\infty r_1^2 r_2^2 e^{-4r_1} e^{-4r_2} \delta(r_1 - r_2)\, dr_1 dr_2$$

$$= \frac{64}{\pi^2} \int_0^\infty r_1^4 e^{-8r_1} dr_1 = \frac{64}{\pi^2} \frac{3}{4096} = \frac{64}{\pi^2}(.000732)$$

Actually there is an additional factor of $(4\pi)^2$ due to the angular integration

So $E^{(1)} = \frac{64(16)3}{4096} = \frac{3}{4}$ au $\rightarrow 20.41$ eV

So $E^{(0)} + E^{(1)} = -108.84 + 20.41 = -80.43$ eV.