Phy 491 HW 2

Problem 2.1 Assume Li can be treated as a hydrogen-like multi-electron atom (electron configuration $1s^2 2s^1$) in which the 1s shell screens the nuclear charge.

2.1.1 Calculate its first ionization energy (removing the 2s electron) and discuss why this result differs from the experimentally observed value of 5.4 eV. (3 Points)

2.1.2 Calculate the 3rd ionization energy of the Li atom. Why/why not is this calculation exact? (3 Points)

2.1.1

If we assume the first two $1s$ electrons completely screen out $2e^+$ from the nucleus and leave $z = 1$, our calculations would be the same as hydrogen only with a greater central mass, and end up pretty close to $13.6eV$ However, the 2s electron is in the second energy level, so using the energy eigenvalue equation for hydrogen

$$E_n = -\frac{1}{2(n)^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2\frac{m_e c^2}{\hbar^2}$$

the energy eigenvalue for the orbital would actually be

$$E_2 = -\frac{1}{8}\left(\frac{1*e^2}{4\pi\epsilon_0}\right)^2\frac{m_e c^2}{\hbar^2} = -\frac{1}{4}*13.6eV = -3.4eV$$

This is smaller than the experimentally ovserved value due to the assumptions we used. Particularly, the assumption that the nucleus is fully shielded by the $1s$ electrons. The $2s$ orbital actually is partially beneath the $1s$ orbital, so the actual charge seen by the $2s$ electron is greater.

2.1.2 Using the eigenvalue equation above and the fact that this electron is in the $1s$ orbital, this yields

$$E_1 = -\frac{1}{2}\left(\frac{3e^2}{4\pi\epsilon_0}\right)^2\frac{m_e c^2}{\hbar^2} = -\frac{3^2}{1}*13.6eV = -122.4eV$$

The calculation is exact at least to the decimal value we're concerned about. The shielding effect is no longer in place and there aren't any electron-electron interactions now.

Problem 2.2 Kr^{35+} is a an ion with only one remaining 1s electron and a nuclear radius of $R = 4.19fm$.

2.2.1 Assuming a hydrogenic ground state wavefunction (n=1, l=0, m=0) with Bohr radius a_0, calculate the probability to find the electron inside the nucleus. (5 Points)

Kr^{35+} is quite ionized.

Assuming a hydrogen Bohr radius a_0 and hydrogenic ground state, we can use the radial wave function equation found in Mcintyre (and various neat tables) to approximate the wave

function.

$$Z = 36$$
$$a_0 = 0.0529nm = 0.0529 * 10^{-9}m = 52.9 * 10^{-12}m$$
$$R = 4.19fm = 4.19 * 10^{-12}m \quad \Psi_{100}(r, \theta, \phi) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}e^{-Zr/a_0}$$

To find the probabilty of finding Ψ inside the nucleus, we need only integrate this function for the volume of the sphere $r < R$

$$\int_V |\Psi_{100}|^2 dV = 4\pi \int_0^R r^2 \left[\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}e^{-Zr/a_0}\right]^2 dr$$
$$= 4\left(\frac{Z}{a_0}\right)^3 \int_0^R r^2 e^{-2Zr/a_0} dr$$

By the power of Wolfram

Definite integral

$$\int_0^R r^2 e^{-(2Zr)/a} dr = \frac{a\left(a^2 - e^{-(2RZ)/a}\left(a^2 + 2aRZ + 2R^2Z^2\right)\right)}{4Z^3}$$

$$= \frac{1}{a_0^3}\left[a_0^3 - a_0 e^{-2RZ/a_0}\left(a_0^2 + 2a_0 RZ + 2R^2 Z^2\right)\right]$$
$$= 1 - e^{-2RZ/a_0}\left(1 + \frac{2RZ}{a_0} + \frac{2R^2Z^2}{a_0^2}\right)$$

For a very large RZ/a_0 this blows up, and for a very small RZ/a_0 it approaches zero, which makes sense.

$$\frac{RZ}{a_0} = \frac{4.19 * 36}{52.9} = 2.85$$
$$\int_V |\Psi_{100}|^2 dV = 1 - e^{-5.70}\left(1 + 5.70 + 16.26\right) = 0.923$$

There is a 92% chance of observing the electron inside of the Kr nucleus. What that means physically? I have no idea. Maybe a good question for office hours.

Problem 2.3 Any region of space in which the kinetic energy of a particle would become negative is classically forbidden. For a hydrogen atom in its ground state

2.3.1 Find the classically forbidden region. (3 points)

2.3.2 Calculate the quantum mechanical probability to find the electron in this forbidden region. (6 points)

Classically forbidden: $KE < 0$

2.3.1

An electron in its ground state has total energy $E_1 = -13.6eV$, so the classically forbidden region is anywhere where potential energy is $-13.6eV$ or greater. This occurs for $U(r) = -\frac{ke^2}{r} > -13.6eV$ aka beyond the bohr radius $a_0 = 52.9 * 10^{-12}m$

2.3.2

This is the portion of the wavefunction where $r > a_0$, so piggybacking off our previous formulas

$$\int_V |\Psi_{100}|^2 dV = 4\left(\frac{Z}{a_0}\right)^3 \int_{a_0}^{\infty} r^2 e^{-2Zr/a_0} dr$$

Definite integral

$$\int_a^{\infty} r^2 e^{-(2Zr)/a} dr = \frac{a^3 e^{-2Z}(2Z(Z+1)+1)}{4Z^3} \quad \text{for } \text{Re}\left(\frac{Z}{a}\right) > 0$$

$$= e^{-2Z}(2Z^2 + 2Z + 1) = 5e^{-2} = 0.677$$

A 67.7% chance. Somewhat unexpected for me but I can reconcile it. In order to have an average value of a_0, it isn't just that there's even probability that the electron is on either side of a_0.

The probability curve is skewed and the exponential drop in value $e^{-Zr/a}$ means that most of the remaining area under the curve is closer to the mean, and the data left of the mean is further away and requires less area to pull it's half of the values down. Hence the difference in probabilites above/below the mean value.