8.6: Other One-Electron Systems

The quantum mechanical treatment of the hydrogen atom can be extended easily to other one-electron systems such as He^{+}, Li^{2+}, etc. The Hamiltonian changes in two places. Most importantly, the potential energy term is changed to account for the charge of the nucleus, which is the atomic number of the atom or ion, Z, times the fundamental unit of charge, e. As shown in Equation 8.6.1, the energy of attraction between the electron and the nucleus increases (i.e., V gets more negative) as the nuclear charge increases.

$$\hat{V}(r) = -\frac{Ze^2}{4\pi\epsilon_0 r} \tag{8.6.1}$$

The other effect is a very slight change in the reduced mass included in the kinetic energy operator. In fact, the larger the nucleus, the better the approximation that the reduced mass is given by the mass of the electron.

Exercise 8.6.1

Compare the reduced mass of the Li^{+2} ion to that of the hydrogen atom.

The effects of the change in V show up in the wavefunctions and the energy eigenvalues. The expression for the energy becomes

$$E_n = -\frac{Z^2\mu e^4}{8\epsilon_0^2 h^2 n^2} = Z^2 E_{n,H} \tag{8.6.2}$$

where $E_{n,H}$ is the energy of the hydrogen atom. The forms of the wavefunctions are identical to those of the hydrogen atom, except for the fact that Z in the radial functions is no longer equal to 1. The selection rules are unchanged, and the Zeeman effect still occurs.

Exercise 8.6.2

Use the orbital energy level expression in Equation 8.6.2 to predict quantitatively the relative energies (in cm^{-1}) of the spectral lines for H and Li^{2+}.

As the plots in Figure 8.6.1 reveal, the increased charge on the nucleus creates a stronger attraction for the electron and thus the electron charge density distributions shift to smaller values of r. These other systems look a lot like compressed hydrogen atoms.

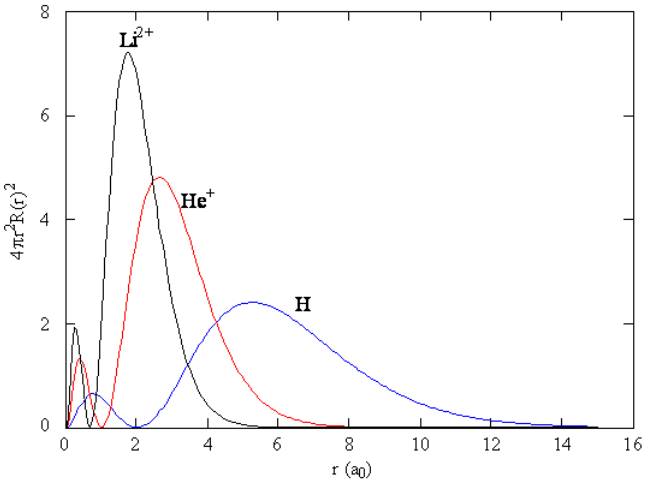

Figure 8.6.1: Radial distribution functions plotted for the 2s orbitals of H (blue), He^{+} (red) and Li^{2+} (black) on the same axis, demonstrating compression of the orbital as Z is increased from 1 to 3.

Exercise 8.6.3

Determine whether or not the angular momentum values, the spherical harmonic functions, and the spectroscopic selection rules that describe the electron in $\hat{H}$ are the same or are different for Li^{2+}. Write a paragraph to justify your answer.