2.31: Some Calculations on the Lithium Atom Ground State

The purpose of this tutorial is to point out that if all that mattered in the determination of atomic structure was energy minimization, the electronic structure of lithium would be $1s_3$, rather than $1s^2 2s^1$.

To deal with this issue we choose the following scaled hydrogenic orbitals for the lithium atom's electrons:

$$\Psi_{1s} = \sqrt{\frac{\alpha^3}{\pi}}\exp(-\alpha,\ \mathrm{r}) \quad \Psi_{2s} = \sqrt{\frac{\alpha^3}{32\pi}}(2 - \alpha\mathrm{r})\exp\left(\frac{-\alpha\mathrm{r}}{2}\right)$$

Using this basis set we find the following expressions (in terms of the variational parameter α) for the expectation values for the various contributions to the electronic energy of the lithium atom.

Nuclear charge:

$$Z = 3$$

Kinetic energy integrals:

$$T_{1s}(\alpha) = \frac{\alpha^2}{2} \quad T_{2s}(\alpha) = \frac{\alpha^2}{8}$$

Electron-nucleus potential energy integrals:

$$V_{N1s}(\alpha) = -Z\alpha \quad V_{N2s}(\alpha) = -\frac{Z}{4}\alpha$$

Electron-electron potential energy integrals:

$$V_{1s1s}(\alpha) = \frac{5}{8}\alpha \quad V_{1s2s}(\alpha) = \frac{17}{81}\alpha$$

We now calculate the ground-state energy of lithium assuming it has the 1s 22s1 electronic configuration. The total electronic energy consists of nine contributions: three kinetic energy terms, three electron-nucleus potential energy terms, and three electron-electron potential energy contriubtions.

$$E_{Li}(\alpha) = 2T_{1s}(\alpha) + 2V_{N1s}(\alpha) + V_{1s1s}(\alpha) + 2T_{2s}(\alpha) + V_{N2s}(\alpha) + 2V_{1s2s}(\alpha)$$

Minimization of the energy with respect to the variational parameter, α, yields the following result:

$$\alpha = \frac{d}{d\alpha}E_{Li}(\alpha) = 0 \ \left|\ \begin{matrix} \text{solve, } \alpha \\ \text{float, 4}\end{matrix}\right. \rightarrow 2.536 \ \ E_{Li}(\alpha) = -7.2333$$

Compared to the experimental ground-state energy -7.478 E_h (the negative of the successive ionization energies of the lithium atom) this result is in error by 3.3%. This result is satisfactory, indicating that the theoretical model has some merit. We could do better, of course, but it would cost something in terms of computational effort and simplicity of the model.

Now we calculate the energy of the hypothetical $1s^3$ electronic configuration for lithium using the same basis functions. Again, the total electronic energy consists of nine contributions: three kinetic energy terms, three electron-nucleus potential energy terms, and three electron-electron potential energy contributions.

$$E_{Li}(\alpha) = 2T_{1s}(\alpha) + 3V_{N1s}(\alpha) + 3V_{1s1s}(\alpha)$$

Minimization of the energy with respect to the variational parameter, α, yields the following result:

First reset the value of α:

$$\alpha = \alpha \ \ \alpha = \frac{d}{d\alpha}E_{Li}(\alpha) = 0 \ \left|\ \begin{matrix} \text{solve, } \alpha \\ \text{float, 4}\end{matrix}\right. \rightarrow 2.375 \quad E_{Li}(\alpha) = -8.4609$$

This electronic configuration has a lower energy than that for $1s^2 2s^1$, and also lower than the experimental value in clear violation of the variational principle.

Electrons are fermions and subject to the Pauli exclusion principle which prevents two electrons from having the same set of quantum numbers. Thus, while the $1s^3$ electronic configuration has a lower energy its existence is prevented by the Pauli principle.