10.29: Electronic Structure - Variational Calculations on the Lithium Atom

The electronic structure of lithium is $1s^2 2s^1$.

One Parameter Estimation

The trial hydrogenic 1s and 2s orbitals are as follows:

$$\psi(1s) = \sqrt{\frac{\alpha^3}{\pi}} e^{-\alpha r} \tag{10.29.1}$$

$$\psi(2s) = \sqrt{\frac{\alpha^3}{32\pi}} (2 - \alpha r) e^{\frac{-\alpha r}{2}} \tag{10.29.2}$$

If these orbitals are used, the variational expression for the lithium atom energy $E(\alpha)$ is given below.

$$E(\alpha) = \alpha^2 - 2Z\alpha + \frac{5}{8}\alpha + \frac{\alpha^2}{8} - \frac{Z\alpha}{4} + \frac{34\alpha}{81} \tag{10.29.3}$$

Minimize energy with respect to the variational parameter, α.

$$\frac{d}{d\alpha} E(\alpha) = 0 \tag{10.29.4}$$

with

- Nuclear charge: $Z = 3$
- Seed value for $\alpha = Z$ for minimization

results in a minimum at $\alpha = 2.5357$ with $E(\alpha) = -7.2333\ E_h$.

This simple one-parameter variational calculation is in error by 3.27% from the experimental value measured by energy necessary to fully ionize the atom (i.e., the sum of the ionization energies in Table A6).

$$E_{exp} = \frac{-5.392\ E_h - 75.638\ E_h - 122.451\ E_h}{27.2114\ E_h} \tag{10.29.5}$$

$$= -7.4778\ E_h \tag{10.29.6}$$

$$\left| \frac{E(\alpha) - E_{exp}}{E_{exp}} \right| = 3.2695\% \tag{10.29.7}$$

As expected the Variational Method estimated energy **always** overestimates the ground state energy (unless the extract wavefunction is describable by the trial wavefunction and then the exact energy is determined).

Two Parameter Estimation

It is possible to improve the results by using a two-parameter calculation in which the 2s electron has a different scale factor that the 1s electrons. In other words the electronic structure would be $1s(\alpha)^2 2s(\beta)^1$.

$$\psi(1s) = \sqrt{\frac{\alpha^3}{\pi}} e^{-\alpha r} \tag{10.29.8}$$

$$\psi(2s) = \sqrt{\frac{\beta^3}{32\pi}} (2 - \beta r) e^{\frac{-\beta r}{2}} \tag{10.29.9}$$

This calculation was first published by E. Bright Wilson (J. Chem. Phys 1, 210 (1933)) in 1933.

- Nuclear charge: $Z = 3$
- Seed values
  - $\alpha = Z$
  - $\beta = Z - 1$ (lower to add a little bit of screening by the 1s electrons)

When the wave function for the $1s(\alpha)^2 2s(\beta)$ electron configuration is written as a Slater determinant, the following variational integrals arise.

$$T_{1s} = \frac{\alpha^2}{2} \tag{10.29.10}$$

$$T_{1s} = \frac{\beta^2}{8} \tag{10.29.11}$$

$$V_{N1a} = -Z\alpha \tag{10.29.12}$$

$$V_{N2s}(\beta) = \frac{-Z\beta}{4} \tag{10.29.13}$$

$$V_{1a1a}(\alpha) = \frac{5}{8}\alpha \tag{10.29.14}$$

$$V_{1s2s}(\alpha, \beta) = \alpha\beta \frac{\beta^4 + 10\alpha\beta^3 + 8\alpha^4 + 20\alpha^3\beta + 12\alpha^2\beta^2}{(2\alpha + \beta)^5} \tag{10.29.15}$$

$$T_{1s2s}(\alpha, \beta) = -4\sqrt{2}\alpha^{\frac{5}{2}}\beta^{\frac{5}{2}} \frac{\beta - 4\alpha}{(2\alpha + \beta)^4} \tag{10.29.16}$$

$$V_{N1a2s}(\alpha, \beta) = \tag{10.29.17}$$

$$V_{1112}(\alpha, \beta) = 32\sqrt{2}\alpha^{\frac{3}{2}}\beta^{\frac{3}{2}} \frac{-28\alpha^3\beta + 264\alpha^4 - 21\alpha\beta^3 - \beta^4 - 86\alpha^2\beta^2}{(2\alpha + \beta)^3(\beta + 6\alpha)^4} \tag{10.29.18}$$

$$V_{1212}(\alpha, \beta) = 16\alpha^3\beta^3 \frac{13\beta^2 + 20\alpha^2 - 30\beta\alpha}{(\beta + 2\alpha)^7} \tag{10.29.19}$$

$$V_{1s2s}(\alpha, \beta) = 32\sqrt{2}\alpha^{\frac{3}{2}}\beta^{\frac{3}{2}} \frac{\alpha - \beta}{(2\alpha + \beta)^4} \tag{10.29.20}$$

The next step in this calculation is to collect these terms in an expression for the total energy of the lithium atom and then minimize it with respect to the variational parameters, α and β. The results of this minimization procedure are shown below

$$E'(\alpha, \beta) = 2T_{1s}(\alpha) + T_{2s}(\beta) - T_{1s}(\alpha)2S_{1s2s}(\alpha\beta)^2 - 2T_{1s2s}(\alpha, \beta)S_{1s2s}(\alpha, \beta)$$

$$+2V_{N1s}(\alpha) + V_{N2s}(\beta) - V_{N1s}(\alpha)S_{1s2s}(\alpha, \beta)^2 - 2V_{N1s2s}(\alpha, \beta)S_{1s2s}(\alpha, \beta)$$

$$+2V_{1s2s}(\alpha, \beta) + V_{1s1s}(\alpha) - 2V_{1112}(\alpha, \beta)S_{1s2s}(\alpha, \beta) - V_{1212}(\alpha, \beta) \tag{10.29.21}$$

$$E''(\alpha, \beta) = 1 - S_{1s2s}\alpha\beta)^2 \tag{10.29.22}$$

$$E(\alpha, \beta) = \frac{E'(\alpha, \beta)}{E''(\alpha, \beta)} \tag{10.29.23}$$

Minimization of $E(\alpha, \beta)$ simultaneously with respect to α and β.

$$\frac{d}{d\alpha}E(\alpha) = \frac{d}{d\alpha}E(\beta) = 0 \tag{10.29.24}$$

results in

- α: 2.6797
- β: 1.8683
- $E(\alpha, \beta)$: $-7.3936\ E_h$

Comparison with experiment value of $-7.4778\ E_h$ in Equation 5:

$$\left|\frac{E(\alpha, \beta) - E_{exp}}{E_{exp}}\right| = 1.1258\% \tag{10.29.25}$$

This result is slightly different from that reported by Wilson in 1933.

- α: 2.686
- β: 1.776
- $E(\alpha, \beta)$: -7.3922

These parameters result in a slight higher energy than those above so it is likely that they did not quite find the energy minimum.

Reference

1. E. Bright Wilson (J. Chem. Phys 1, 210 (1933))

Contributors and Attributions

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