The electronic structure of lithium is $1s^12s^1$. The hydrogenic $1s$ and $2s$ orbitals are as follows:

$$
\begin{align*}
\Psi (1s) &= \sqrt{\frac{\alpha^3}{\pi}} \exp(-\alpha r) \\
\Psi (2s) &= \sqrt{\frac{\alpha^3}{32\pi}} (2-\alpha r) \exp\left(-\frac{\alpha r}{2}\right)
\end{align*}
$$

If these orbitals are used the variational expression for the lithium atom energy is given below.

Nuclear charge:

\[ Z = 3 \]

Seed value for $\alpha$:

\[ \alpha = Z \]

Define variational integral for lithium:

\[
E (\alpha) = \alpha^2 - 2Z\alpha + \frac{5}{8}\alpha + \frac{\alpha^2}{8} - \frac{Z\alpha}{4} + \frac{34\alpha}{81}
\]

Minimize energy with respect to the variational parameter, $\alpha$:

\[
\begin{align*}
\text{Given } \frac{d}{d\alpha} E (\alpha) &= 0 & \alpha &= \text{Find} (\alpha) & \alpha &= 2.5357 & E (\alpha) &= -7.2333 \\
\end{align*}
\]

This one-parameter variational calculation is in error by 3.27%. The ground state energy is the negative of the sum of the ionization energies.

\[
E_{\text{exp}} = \frac{-5.392-75.638-122.451}{27.2114} = -7.4778
\]

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 $1s(\alpha)^22s(\beta)^1$.

This calculation was first published by E. Bright Wilson \textit{(J. Chem. Phys 1, 210 (1933))} in 1933. Levine's Quantum Chemistry (6th ed. p 299) contains a brief summary of the calculation.
When the wave function for the $1s(\alpha)^22s(\beta)$ electron configuration is written as a Slater determinant, the following variational integrals arise.

\[
\begin{align*}
T_{1s}(\alpha) &= \frac{\alpha^2}{2} & T_{2s}(\beta) &= \frac{\beta^2}{2} & V_{N1s}(\alpha) &= -Z\alpha \\
V_{N2s}(\beta) &= \frac{-Z\beta}{4} \\
V_{1s1s}(\alpha) &= \frac{5}{8}\alpha \\
V_{1s2s}(\alpha,\beta) &= \frac{\beta^4 + 10\alpha\beta + 8\alpha^4 + 20\alpha^3\beta + 12\alpha^2\beta^2}{(2\alpha + \beta)^5} \\
T_{1s2s}(\alpha,\beta) &= -4\sqrt{4}\alpha^{\frac{5}{2}}\beta^{\frac{5}{2}}\frac{\beta - 4\alpha}{(2\alpha + \beta)^4} \\
V_{N1s2s}(\alpha,\beta) &= -Z4\sqrt{2}\alpha^{\frac{3}{2}}\beta^{\frac{3}{2}}\frac{2\alpha - \beta}{(2\alpha + \beta)^3} \\
V_{1112}(\alpha,\beta) &= 32\sqrt{2}\beta^{\frac{3}{2}}\alpha^{\frac{5}{2}}\frac{-28\alpha^3\beta + 264\alpha^4 - 21\alpha\beta^3 - \beta^4 - 86\alpha^2\beta^2}{(2\alpha\beta)^3(\beta + 6\alpha)^4} \\
V_{1212}(\alpha,\beta) &= 16\alpha^3\beta^3\frac{13\beta^2 + 20\alpha^2 - 30\beta\alpha}{(\beta + 2\alpha)^7} \\
S_{1s2s}(\alpha,\beta) &= 32\sqrt{2}\alpha^{\frac{3}{2}}\beta^{\frac{3}{2}}\frac{\alpha - \beta}{(2\alpha + \beta)^4}
\end{align*}
\]

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, $\alpha$ and $\beta$. The results of this minimization procedure are shown below.

\[
E(\alpha,\beta) = \frac{2T_{1s}(\alpha) + T_{2s}(\beta) - T_{1s}(\alpha)S_{1s2s}(\alpha,\beta)^2 - 2T_{1s2s}(\alpha,\beta)S_{1s2s}(\alpha,\beta) ... + 2V_{N1s}(\alpha) + V_{N2s}(\beta) - V_{N1s}(\alpha)S_{1s2s}(\alpha,\beta)^2 - 2V_{N1s2s}(\alpha,\beta)S_{1s2s}(\alpha,\beta) ... + 2V_{1s2s}(\alpha,\beta) + V_{1s1s}(\alpha) - 2V_{1112}(\alpha,\beta)S_{1s2s}(\alpha,\beta) - V_{1212}(\alpha,\beta) + V_{1112}(\alpha,\beta)S_{1s2s}(\alpha,\beta) - V_{1212}(\alpha,\beta)S_{1s2s}(\alpha,\beta) - 1 - S_{1s2s}(\alpha,\beta)^2}{1 - S_{1s2s}(\alpha,\beta)^2}
\]

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

\[
\text{Given} & \quad \frac{d}{d\alpha} E(\alpha,\beta) = 0 \quad \frac{d}{d\beta} E(\alpha,\beta) = 0 \quad \text{Find} \quad \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} 2.6797 \\ 1.8683 \end{pmatrix} \quad E(\alpha,\beta) = -7.3936
\]

Comparison with experiment (ground state energy is the negative of the sum of the ionization energies):

\[
\text{E}_{\exp} = \frac{-5.392 - -75.638 - -122.451}{27.2114} \quad E_{\exp} = -7.4778 \quad E(\alpha,\beta) - E_{\exp} = 1.1258 \% \quad \text{end(matrix)}
\]

This result is slightly different from that reported by Wilson in 1933. He found that the energy was minimized at $-7.3922\ E_h$, with parameters $\alpha = 2.686$ and $\beta = 1.776$. When I use his parameters with my equation for the energy I get Wilson's energy value, so I can only conclude that he did not quite find the energy minimum.
\[
\begin{bmatrix}
\alpha = 2.686 & \beta = 1.776 & E (\alpha, \beta) = -7.3922
\end{bmatrix}
\]