Approximation of the Ground-State Total Energy of a Lithium Atom © Thursday, March 27, 2025, by James Pate Williams, Jr., BA, BS, Master of Software Engineering, PhD

In this paper we approximate the ground-state energy of the lithium atom which has the atomic number Z = 3. The neutral atom has three protons and three electrons. The most common isotopes have three or four neutrons. The ground-state total energy of the lithium atom is -7.4780603234519 Eh in atomic energy units. A very accurate ground-state energy computation for the lithium atom total ground-state energy is in the following document:

get_pdf.cfm

The non-relativistic time-independent Hamiltonian operator of the lithium atom in atomic units is given by the equation:

$$H = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} - \frac{1}{2}\nabla_3^2 - \frac{Z}{r_3} + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}$$

Transformation into spherical coordinates for the first electron is performed as follows:

$$x_1 = r_1 \sin\vartheta_1 \cos\varphi_1, y_1 = r_1 \sin\vartheta_1 \sin\varphi_1, z_1 = r_1 \cos\vartheta_1$$

$$ds_1^2 = dx_1^2 + dy_1^2 + dz_2^1 = dr_1^2 + r_1^2 d\vartheta_1^2 + (r_1 \sin\vartheta_1)^2 d\varphi_1^2$$

$$h_{r_1} = \sqrt{g_{r_1 r_1}} = 1, h_{\vartheta_1} = \sqrt{g_{\vartheta_1\vartheta_1}} = r_1, h_{\varphi_1} = \sqrt{g_{\varphi_1\varphi_1}} = r_1 \sin\vartheta_1$$

Where the g-values are of the orthogonal metric tensor.

$$\begin{aligned}
\nabla_1^2 = {} & \frac{1}{h_{r_1} h_{\vartheta_1} h_{\varphi_1}} \left[\frac{\partial}{\partial r_1}\left(\frac{h_{\vartheta_1} h_{\varphi_1}}{h_{r_1}} \frac{\partial}{\partial r_1}\right) + \frac{\partial}{\partial \vartheta_1}\left(\frac{h_{r_1} h_{\varphi_1}}{h_{\vartheta_1}}\right)\frac{\partial}{\partial \vartheta_1} + \frac{\partial}{\partial \varphi_1}\left(\frac{h_{r_1} h_{\vartheta_1}}{h_{\varphi_1}}\right)\frac{\partial}{\partial \varphi_1}\right] \\
& = \frac{1}{r_1^2 \sin\vartheta_1}\frac{\partial}{\partial r_1}\left(r_1^2 \sin\vartheta_1 \frac{\partial}{\partial r_1}\right) + \frac{1}{r_1^2 \sin\vartheta_1}\frac{\partial}{\partial \vartheta_1}\left(\frac{r_1 \sin\vartheta_1}{r_1}\frac{\partial}{\partial \vartheta_1}\right) \\
& + \frac{1}{r_1^2 \sin\vartheta_1}\frac{\partial}{\partial \varphi_1}\left(\frac{r_1}{r_1 \sin\vartheta_1}\frac{\partial}{\partial \varphi_1}\right) \\
& = \frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2 \frac{\partial}{\partial r_1}\right) + \frac{1}{r_1^2 \sin\vartheta_1}\frac{\partial}{\partial \vartheta_1}\left(\sin\vartheta_1 \frac{\partial}{\partial \vartheta_1}\right) + \frac{1}{(r_1 \sin\vartheta_1)^2}\frac{\partial^2}{\partial \varphi_1^2}
\end{aligned}$$

Suppose the wavefunction for the first electron is of the form:

$$\psi_1(r_1, \vartheta_1, \varphi_1, \zeta_1) = R_1(r_1, \zeta_1)\Theta_1(\vartheta_1, \varphi_1)$$

$$-\frac{1}{2}\nabla_1^2 \psi_1 - \frac{\zeta_1}{r_1}\psi_1 = E_1 \psi_1$$

$$\frac{1}{r_1^2 R_1}\frac{\partial}{\partial r_1}\left(r_1^2 \frac{\partial R_1}{\partial r_1}\right) + \frac{1}{r_1^2 \sin\vartheta_1 \Theta_1}\frac{\partial}{\partial \vartheta_1}\left(\sin\vartheta_1 \frac{\partial \Theta_1}{\partial \vartheta_1}\right) + \frac{1}{(r_1 \sin\vartheta_1)^2 \Theta_1}\frac{\partial^2 \Theta_1}{\partial \varphi_1^2} - \frac{3}{r_1} = E_1$$

Multiplying through the first radial coordinate squared yields:

$$\frac{1}{R_1}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial R_1}{\partial r_1}\right)+\frac{1}{\sin\vartheta_1\Theta_1}\frac{\partial}{\partial\vartheta_1}\left(\sin\vartheta_1\frac{\partial\Theta_1}{\partial\vartheta_1}\right)+\frac{1}{(\sin\vartheta_1)^2\Theta_1}\frac{\partial^2\Theta_1}{\partial\varphi_1^2}-\zeta_1 r_1=r_1^2E_1$$

After regrouping the previous wave equation, we have:

$$\frac{1}{R_1}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial R_1}{\partial r_1}\right)-\zeta_1 r_1-r_1^2E_1=-\frac{1}{\sin\vartheta_1\Theta_1}\frac{\partial}{\partial\vartheta_1}\left(\sin\vartheta_1\frac{\partial\Theta_1}{\partial\vartheta_1}\right)-\frac{1}{(\sin\vartheta_1)^2\Theta_1}\frac{\partial^2\Theta_1}{\partial\varphi_1^2}$$

Let the Greek letter lambda be a separation constant:

$$\frac{1}{R_1}\frac{d}{dr_1}\left(r_1^2\frac{dR_1}{dr_1}\right)-\zeta_1 r_1-r_1^2E_1=\lambda_1$$

$$-\frac{1}{\sin\vartheta_1\Theta_1}\frac{\partial}{\partial\vartheta_1}\left(\sin\vartheta_1\frac{\partial\Theta_1}{\partial\vartheta_1}\right)-\frac{1}{(\sin\vartheta_1)^2\Theta_1}\frac{\partial^2\Theta_1}{\partial\varphi_1^2}=\lambda_1$$

$$\frac{d}{dr_1}\left(r_1^2\frac{dR_1}{dr_1}\right)-\zeta_1 r_1R_1-r_1^2E_1R_1-\lambda_1R_1=0$$

$$\frac{1}{\sin\vartheta_1}\frac{\partial}{\partial\vartheta_1}\left(\sin\vartheta_1\frac{\partial\Theta_1}{\partial\vartheta_1}\right)+\frac{1}{(\sin\vartheta_1)^2}\frac{\partial^2\Theta_1}{\partial\varphi_1^2}+\lambda_1\Theta_1=0$$

$$\sin\vartheta_1\frac{\partial}{\partial\vartheta_1}\left(\sin\vartheta_1\frac{\partial\Theta_1}{\partial\vartheta_1}\right)+\frac{\partial^2\Theta_1}{\partial\varphi_1^2}+\lambda_1(\sin\vartheta_1)^2\Theta_1=0$$

Separating the theta and phi variables gives rise to the equation:

$$\sin\vartheta_1\frac{\partial}{\partial\vartheta_1}\left(\sin\vartheta_1\frac{\partial\Theta_1}{\partial\vartheta_1}\right)+\lambda_1(\sin\vartheta_1)^2\Theta_1=-\frac{\partial^2\Theta_1}{\partial\varphi_1^2}$$

$$\Theta_1(\vartheta_1,\varphi_1)=Y_1(\vartheta_1,\varphi_1)\Phi_1(\varphi_1)$$

$$\frac{1}{Y_1}\left[\sin\vartheta_1\frac{\partial}{\partial\vartheta_1}\left(\sin\vartheta_1\frac{\partial Y_1}{\partial\vartheta_1}\right)+\lambda_1(\sin\vartheta_1)^2\right]=-\frac{1}{\Phi_1}\frac{\partial^2\Phi_1}{\partial\varphi_1^2}=m_1^2$$

$$\sin\vartheta_1\frac{d}{d\vartheta_1}\left(\sin\vartheta_1\frac{dY_1}{d\vartheta_1}\right)+\lambda_1(\sin\vartheta_1)^2\mathrm{Y}_1-m_1^2\mathrm{Y}_1=0$$

$$\frac{d^2\Phi_1}{d\varphi_1^2}+m_1^2\Phi_1=0$$

We call the integer quantum number, m, the magnetic quantum number.

$$\Phi_1(\varphi_1)=\frac{1}{\sqrt{2\pi}}e^{im_1\varphi_1}$$

$$\frac{1}{\sin\vartheta_1}\frac{d}{d\vartheta_1}\left(\sin\vartheta_1\frac{dY_1}{d\vartheta_1}\right)+\left[\lambda_1-\frac{m_1^2}{(\sin\vartheta_1)^2}\right]\mathrm{Y}_1=0$$

Next, we define the angular quantum number as follows:

$$\lambda_1=l_1(l_1+1)$$

$$Y_{1,l_1m_1}(\vartheta_1,\varphi_1)=\epsilon\left[\frac{2l_1+1}{4\pi}\frac{(l_1-|m_1|)!}{(l_1+|m_1|)!}\right]^{1/2}P_{l_1}^{m_1}(\cos\vartheta_1)e^{im_1\varphi_1},\epsilon=(-1)^m\forall m>0,\epsilon=1\forall m\leq 0$$

$$Y_{1,00}=\frac{1}{\sqrt{4\pi}}$$

$$Y_{1,10}=\left(\frac{3}{4\pi}\right)^{1/2}\cos\vartheta_1$$

$$Y_{1,1\pm1}=\mp\left(\frac{3}{8\pi}\right)^{1/2}\sin\vartheta_1 e^{\pm i\varphi_1}$$

$$Y_{1,20}=\left(\frac{5}{16\pi}\right)^{1/2}[3(\cos\vartheta_1)^2-1]$$

$$Y_{2,1\pm1}=\mp\left(\frac{15}{8\pi}\right)^{1/2}\sin\vartheta_1\cos\vartheta_1\,e^{\pm i\varphi_1}$$

$$Y_{1,2\pm2}=\left(\frac{15}{32\pi}\right)^{1/2}(\sin\vartheta_1)^2e^{\pm 2i\varphi_1}$$

The above spherical harmonics are from ***Quantum Mechanics Third Edition*** © 1968 by Leonard I. Schiff page 80.

$$-\frac{1}{2r_1^2}\frac{d}{dr_1}\left(r_1^2\frac{dR_1}{dr_1}\right)-\frac{\zeta_1}{r_1}R_1+\frac{l_1(l_1+1)}{2r_1^2}R_1=E_1R_1$$

$$E_1=-\frac{\zeta_1^2}{2n_1^2}$$

$$R_{1,n_1l_1}(r_1,Z)=-\left\{\left(\frac{2\zeta_1}{n_1}\right)^3\frac{(n_1-l_1-1)!}{2n_1[(n_1+l_1)!]^3}\right\}^{1/2}e^{-\rho_1/2}{\rho_1}^{l_1}L_{n_1+l_1}^{2l_1+1}(\rho_1)$$

$$\rho_1=\frac{2\zeta_1}{n_1}r_1$$

Let the ground-state wavefunction of lithium be as follows [electron configuration 1s(2)2s(1)]:

$$\Psi(\vec{r},\vec{\zeta}) = \frac{1}{\sqrt{6}}\begin{vmatrix} a(1) & a(2) & a(3) \\ b(1) & b(2) & b(3) \\ c(1) & c(2) & c(3) \end{vmatrix}$$

$$= \frac{1}{\sqrt{6}}[a(1)b(2)c(3) + a(2)b(3)c(1) + a(3)b(1)c(2) - a(2)b(1)c(3) - a(1)b(3)c(2) - a(3)b(2)c(1)]$$

Where (see for derivatives ***Quantum Chemistry Second Edition*** © 1974 by Ira N. Levine):

$$a(1) = R_{10}(r_1,\zeta_1)Y_{1,00}(\vartheta_1,\varphi_1) = -2\zeta_1^{3/2}e^{-\zeta_1 r_1}\frac{1}{\sqrt{4\pi}}$$

$$a(2) = R_{10}(r_2,\zeta_2)Y_{1,00}(\vartheta_2,\varphi_2) = -2\zeta_2^{3/2}e^{-\zeta_2 r_2}\frac{1}{\sqrt{4\pi}}$$

$$a(3) = R_{10}(r_3,\zeta_3)Y_{1,00}(\vartheta_3,\varphi_3) = -2\zeta_3^{3/2}e^{-\zeta_3 r_3}\frac{1}{\sqrt{4\pi}}$$

$$b(1) = R_{10}(r_1,\zeta_1)Y_{1,00}(\vartheta_1,\varphi_1) = -2\zeta_1^{3/2}e^{-\zeta_1 r_1}\frac{1}{\sqrt{4\pi}}$$

$$b(2) = R_{10}(r_2,\zeta_2)Y_{1,00}(\vartheta_2,\varphi_2) = -2\zeta_2^{3/2}e^{-\zeta_2 r_2}\frac{1}{\sqrt{4\pi}}$$

$$b(3) = R_{10}(r_3,\zeta_3)Y_{1,00}(\vartheta_3,\varphi_3) = -2\zeta_3^{3/2}e^{-\zeta_3 r_3}\frac{1}{\sqrt{4\pi}}$$

$$c(1) = R_{20}(r_1,\zeta_1)Y_{1,00}(\vartheta_1,\varphi_1) = -\left(\frac{\zeta_1}{2}\right)^{3/2}(2-\zeta_1 r_1)e^{-\zeta_1 r_1/2}\frac{1}{\sqrt{4\pi}}$$

$$c(2) = R_{20}(r_2,\zeta_2)Y_{1,00}(\vartheta_2,\varphi_2) = -\left(\frac{\zeta_2}{2}\right)^{3/2}(2-\zeta_2 r_2)e^{-\zeta_2 r_2/2}\frac{1}{\sqrt{4\pi}}$$

$$c(3) = R_{20}(r_3,\zeta_3)Y_{1,00}(\vartheta_3,\varphi_3) = -\left(\frac{\zeta_3}{2}\right)^{3/2}(2-\zeta_3 r_3)e^{-\zeta_3 r_3/2}\frac{1}{\sqrt{4\pi}}$$

$$-\frac{1}{2r_1^2}\frac{d}{dr_1}\left(r_1^2\frac{dR_{10}}{dr_1}\right) - \frac{\zeta_1}{r_1}R_1 + \frac{l_1(l_1+1)}{2r_1^2}R_{10} = E_1R_{10}$$

$$-\frac{1}{2r_1^2}\left(2r_1\frac{dR_{10}}{dr_1} + r_1^2\frac{d^2R_{10}}{dr_1^2}\right) - \frac{\zeta_1}{r_1}R_{10} + \frac{l_1(l_1+1)}{2r_1^2}R_{10} = E_1R_{10}$$

$$-\frac{1}{2}\frac{d^2R_{10}}{dr_1^2} - \frac{1}{r_1}\frac{dR_{10}}{dr_1} - \frac{\zeta_1}{r_1}R_{10} + \frac{l_1(l_1+1)}{2r_1^2}R_{10} = E_1R_{10}$$

$$\frac{dR_{10}}{dr_1} = 2\zeta_1^{5/2}e^{-\zeta_1 r_1}$$

$$\frac{d^2R_{10}}{dr_1^2} = -2\zeta_1^{7/2}e^{-\zeta_1 r_1}$$

$$\frac{dR_{20}}{dr_1} = -\left(\frac{\zeta_1}{2}\right)^{3/2}\frac{d}{dr_1}(2-\zeta_1 r_1)e^{-\zeta_1 r_1/2} = -\left(\frac{\zeta_1}{2}\right)^{3/2}\left(\frac{-2\zeta_1}{2} - \zeta_1 + \frac{\zeta_1^2}{2}\right)e^{-\zeta_1 r_1/2}$$
$$= -\left(\frac{\zeta_1}{2}\right)^{3/2}\left(2\zeta_1 + \frac{\zeta_1^2}{2}\right)e^{-\zeta_1 r_1/2}$$

$$\frac{d^2R_{20}}{dr_1^2} = -\left(\frac{\zeta_1}{2}\right)^{3/2}\left(\frac{\zeta_1^2}{2} + \frac{\zeta_1^2}{2} - \frac{\zeta_1^3}{4}\right)e^{-\zeta_1 r_1/2} = -\left(\frac{\zeta_1}{2}\right)^{3/2}\left(\zeta_1^2 - \frac{\zeta_1^3}{4}\right)e^{-\zeta_1 r_1/2}$$

$$-\iiint\iiint\iiint [a(1)b(2)c(3)]\frac{1}{2}\frac{d^2}{dr_1^2}[a(1)b(2)c(3)]r_1^2dr_1d\vartheta_1d\varphi_1r_2^2dr_2d\vartheta_2d\varphi_2r_3^2dr_3d\vartheta_3d\varphi_3$$
$$= -\iiint a(1)\frac{1}{2}\frac{d^2}{dr_1^2}a(1)r_1^2dr_1d\vartheta_1d\varphi_1$$
$$= -\frac{4\zeta_1^7}{2}\int_0^\infty e^{-2\zeta_1 r_1}r_1^2dr_1 = -\frac{4\zeta_1^7}{(2\zeta_1)^3} = -\frac{\zeta_1^4}{2}$$

$$-\iiint\iiint\iiint [a(1)b(2)c(3)]\frac{1}{r_1}\frac{d}{dr_1}[a(1)b(2)c(3)]r_1^2dr_1d\vartheta_1d\varphi_1r_2^2dr_2d\vartheta_2d\varphi_2r_3^2dr_3d\vartheta_3d\varphi_3$$
$$= -\iiint a(1)\frac{1}{r_1}\frac{d}{dr_1}a(1)r_1^2dr_1d\vartheta_1d\varphi_1 = -4\zeta_1^5\int_0^\infty e^{-2\zeta_1 r_1}r_1dr_1 = -4\zeta_1^5\frac{1}{(2\zeta_1)^2}$$
$$= \zeta_1^3$$

$$\iiint\iiint\iiint [a(1)b(2)c(3)]\frac{\zeta_1}{r_1}[a(1)b(2)c(3)]r_1^2dr_1d\vartheta_1d\varphi_1r_2^2dr_2d\vartheta_2d\varphi_2r_3^2dr_3d\vartheta_3d\varphi_3$$
$$= \iiint a(1)\frac{\zeta_1}{r_1}a(1)r_1^2dr_1d\vartheta_1d\varphi_1 = \zeta_1\int_0^\infty e^{-2\zeta_1 r_1}\,r_1dr_1 = \frac{\zeta_1}{(2\zeta_1)^2} = \frac{1}{4\zeta_1}$$

$$\iiint\iiint\iiint [a(1)b(2)c(3)]\frac{l_1(l_1+1)}{2r_1^2}[a(1)b(2)c(3)]r_1^2dr_1d\vartheta_1d\varphi_1r_2^2dr_2d\vartheta_2d\varphi_2r_3^2dr_3d\vartheta_3d\varphi_3$$
$$= \iiint a(1)\frac{l_1(l_1+1)}{2r_1^2}a(1)r_1^2dr_1d\vartheta_1d\varphi_1 = \frac{l_1(l_1+1)}{2}\int_0^\infty e^{-2\zeta_1 r_1}\,dr_1 = \frac{l_1(l_1+1)}{2}\frac{1}{2\zeta_1}$$
$$= \frac{l_1(l_1+1)}{4\zeta_1}$$

$$E_{1,KE} = -\frac{\zeta_1^4}{2} + \frac{l_1(l_1+1)}{4\zeta_1} - \frac{\zeta_1^2}{2n_1^2}$$

$$E_{1,PE} = -\frac{Z}{4\zeta_1}$$

$$E_{2,KE} = -\frac{\zeta_2^4}{2} + \frac{l_2(l_2+1)}{4\zeta_2} - \frac{\zeta_2^2}{2n_2^2}$$

$$E_{2,PE} = -\frac{Z}{4\zeta_2}$$

$$\iiint \iiint \iiint [a(1)b(2)c(3)] \frac{d^2}{dr_3^2} [a(1)b(2)c(3)] r_1^2 dr_1 d\vartheta_1 d\varphi_1 r_2^2 dr_2 d\vartheta_2 d\varphi_2 r_3^2 dr_3 d\vartheta_3 d\varphi_3$$
$$= \iiint c(3) \frac{d^2}{dr_3^2} c(3) r_3^2 dr_3 d\vartheta_3 d\varphi_3 = \left(\frac{\zeta_3}{2}\right)^3 \left(\zeta_3^2 - \frac{\zeta_3^3}{4}\right) \int_0^\infty e^{-\zeta_3 r_3/2} r_3^2 dr_3$$
$$= \left(\frac{\zeta_3}{2}\right)^3 \left(\zeta_3^2 - \frac{\zeta_3^3}{4}\right) \frac{2!}{\left(\frac{\zeta_3}{2}\right)^3}$$

$$E_{3,KE}$$
$$= -\left(\frac{\zeta_3}{2}\right)^3 \left(\zeta_3^2 - \frac{\zeta_3^3}{4}\right) \frac{2!}{\left(\frac{\zeta_3}{2}\right)^3}$$
$$- \iiint \iiint \iiint [a(1)b(2)c(3)] \frac{1}{r_3} \frac{d}{dr_3} [a(1)b(2)c(3)] r_1^2 dr_1 d\vartheta_1 d\varphi_1 r_2^2 dr_2 d\vartheta_2 d\varphi_2 r_3^2 dr_3 d\vartheta_3 d\varphi_3$$
$$= -2\left(\zeta_3^2 - \frac{\zeta_3^3}{4}\right) - \left[\int_0^\infty \left(\frac{\zeta_3}{2}\right)^{3/2} (2 - \zeta_3 r_3) e^{-\zeta_3 r_3/2} \frac{1}{r_3} \left(\frac{\zeta_3}{2}\right)^{3/2} \left(2\zeta_3 + \frac{\zeta_3^2}{2}\right) e^{-\zeta_3 r_3/2} r_3^2 dr_3\right] - \frac{\zeta_3^2}{2n_3^2}$$

$$E_{3,PE} = -\frac{Z}{4\zeta_3}$$

We use the Monte Carlo method of integration without the Metropolis-Hastings heuristic.

$$E_{1,EE}$$
$$= \iiint \iiint \iiint [a(1)b(2)c(3)] \frac{1}{r_{12}} [a(1)b(2)c(3)] r_1^2 dr_1 d\vartheta_1 d\varphi_1 r_2^2 dr_2 d\vartheta_2 d\varphi_2 r_3^2 dr_3 d\vartheta_3 d\varphi_3$$
$$= \iiint \iiint [a(1)b(2)] \frac{1}{r_{12}} [a(1)b(2)] r_1^2 dr_1 d\vartheta_1 d\varphi_1 r_2^2 dr_2 d\vartheta_2 d\varphi_2$$
$$= \int_0^\infty \int_0^\infty [a(1)b(2)] \frac{1}{r_{12}} [a(1)b(2)] r_1^2 dr_1\, r_2^2 dr_2$$

$$E = \iiint \iiint \iiint \Psi(\vec{r},\vec{\zeta}) H \Psi(\vec{r},\vec{\zeta})\, r_1^2 dr_1 d\vartheta_1 d\varphi_1 r_2^2 dr_2 d\vartheta_2 d\varphi_2 r_3^2 dr_3 d\vartheta_3 d\varphi_3$$
$$= \frac{1}{6} \iiint \iiint \iiint [a(1)b(2)c(3) + a(2)b(3)c(1) + a(3)b(1)c(2) - a(2)b(1)c(3) - a(1)b(3)c(2) - a(3)b(2)c(1)] H [a(1)b(2)c(3) + a(2)b(3)c(1) + a(3)b(1)c(2) - a(2)b(1)c(3) - a(1)b(3)c(2) - a(3)b(2)c(1)] r_1^2 dr_1 d\vartheta_1 d\varphi_1 r_2^2 dr_2 d\vartheta_2 d\varphi_2 r_3^2 dr_3 d\vartheta_3 d\varphi_3$$

$$\begin{aligned} E = {} & (123)H(123) + (123)H(231) + (123)H(312) - (123)H(213) - (123)H(132) \\ & - (123)H(321) + (231)H(123) + (231)H(231) + (231)H(312) \\ & - (231)H(213) - (231)H(132) - (231)H(321) + (312)H(123) \\ & + (312)H(231) + (312)H(312) - (312)H(213) - (312)H(132) \\ & - (312)H(321) - (213)H(123) - (213)H(231) - (213)H(312) \\ & + (213)H(213) + (213)H(132) + (213)H(321) - (132)H(123) \\ & - (132)H(231) - (132)H(312) + (132)H(213) + (132)H(132) \\ & + (132)H(321) - (321)H(123) - (321)H(231) - (321)H(312) \\ & + (321)H(213) + (321)H(132) + (321)H(321) \end{aligned}$$

$$E = \sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{k=1}^{3}\sum_{l=1}^{3}\sum_{m=1}^{3}\sum_{n=1}^{3} (ijk)H(lmn)$$
$$= \sum_{i=1}^{3}\sum_{j=1}^{3}\sum_{k=1}^{3}\sum_{l=1}^{3}\sum_{m=1}^{3}\sum_{n=1}^{3} \left[\delta_{il}(i)H_i(l) + \delta_{jm}(j)H_j(m) + \delta_{kn}(k)H_k(n)\right]$$

$$H_i = -\frac{1}{2}\nabla_i^2 - \frac{3}{r_i} + \sum_{i=1}^{3}\sum_{j=i+1}^{3}\frac{1}{r_{ij}}$$

We use an elitist evolutionary hill climber to compute the zeta values (Slater atomic orbital screening variables.

Best application execution is on the next page:

Lithium Atom (Li, Z = 3)
Best Ground-State Energy in the literature:
-7.4780603234519 Eh
Generations = 100, Population = 25
STL C++ Mersenne Twister PRNG Seed = 1
Randomized Monte Carlo Integration
Number of Integration Steps = 4,000,000

#	Kinetic	Potential	EE	Total	% Error
0	-16.051631	-0.858407	9.457497	-7.452541	0.341255
19	-14.858569	-0.921560	8.094672	-7.685457	2.773398

#	Zeta 1	Zeta 2	Zeta 3
0	2.997185	2.932557	2.128124
19	2.956536	2.260979	2.231015

Runtime (in Seconds): 400.625000