Approximation of the Ground-State Total Energy of a Beryllium Atom © Sunday, March 30 to Tuesday April 1, 2025, by James Pate Williams, Jr., BA, BS, Master of Software Engineering, PhD Computer Science

In this paper we approximate the non-relativistic ground-state energy of a beryllium atom which has the atomic number Z = 4. Beryllium is the first alkaline earth metal in the periodic table (Group 2 IIA, Period 2). The neutral atom has four protons and four electrons. The most common isotope has five neutrons. Perhaps the best theoretical non-relativistic ground-state total energy of the beryllium atom is -14.667356508 Eh in atomic energy units and is from the online paper in TABLE II:

Ground and excited $^1\!S$ states of the beryllium atom

The experimental ground-state energy is -399.14863859 eV = -14.66843631 Eh and is computed from the NIST Spectroscopic Data at:

NIST Atomic Ionization Energies Output

NIST_periodictable_June24_iupac.pdf

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

$$H=-\frac{1}{2}\nabla_1^2-\frac{Z}{r_1}-\frac{1}{2}\nabla_2^2-\frac{Z}{r_2}-\frac{1}{2}\nabla_3^2-\frac{Z}{r_3}-\frac{1}{2}\nabla_4^2-\frac{Z}{r_4}+\frac{1}{r_{12}}+\frac{1}{r_{13}}+\frac{1}{r_{14}}+\frac{1}{r_{23}}+\frac{1}{r_{24}}+\frac{1}{r_{34}}$$

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

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

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

$$h_{r_1}=\sqrt{g_{r_1r_1}}=1, h_{\vartheta_1}=\sqrt{g_{\vartheta_1\vartheta_1}}=r_1, h_{\varphi_1}=\sqrt{g_{\varphi_1\varphi_1}}=r_1\sin\vartheta_1$$

Where the g-values are of the orthogonal metric tensor. The Laplacian operator in any orthogonal coordinate system is:

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

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

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

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

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

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:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

```
Enter the atomic number Z (2 to 6 or 0 to quit): 4
24      12      0       +       a(1)b(2)c(3)d(4)
23      11      1       -       a(1)b(2)c(4)d(3)
22      11      1       -       a(1)b(3)c(2)d(4)
21      10      0       +       a(1)b(3)c(4)d(2)
20      10      0       +       a(1)b(4)c(2)d(3)
19      9       1       -       a(1)b(4)c(3)d(2)
18      9       1       -       a(2)b(1)c(3)d(4)
17      8       0       +       a(2)b(1)c(4)d(3)
16      8       0       +       a(2)b(3)c(1)d(4)
15      7       1       -       a(2)b(3)c(4)d(1)
14      7       1       -       a(2)b(4)c(1)d(3)
13      6       0       +       a(2)b(4)c(3)d(1)
12      6       0       +       a(3)b(1)c(2)d(4)
11      5       1       -       a(3)b(1)c(4)d(2)
10      5       1       -       a(3)b(2)c(1)d(4)
9       4       0       +       a(3)b(2)c(4)d(1)
8       4       0       +       a(3)b(4)c(1)d(2)
7       3       1       -       a(3)b(4)c(2)d(1)
6       3       1       -       a(4)b(1)c(2)d(3)
5       2       0       +       a(4)b(1)c(3)d(2)
4       2       0       +       a(4)b(2)c(1)d(3)
3       1       1       -       a(4)b(2)c(3)d(1)
2       1       1       -       a(4)b(3)c(1)d(2)
1       0       0       +       a(4)b(3)c(2)d(1)
# Even Permutations = 12
```

The theoretical number of even permutations is n! / 2, which in our case is 4! / 2 = 24 / 2 = 12. The a's and b's are 1s orbitals and the c's and d's are 2s orbitals. The first column is the number of transpositions required for full rearrangement. The second column is the number of pairs involved in the rearrangement. The third column is the second column modulo 2 and the fourth column is the sign of the electron configuration.

For the derivatives see ***Quantum Chemistry Second Edition*** © 1974 by Ira N. Levine):

$$a(1) = R_{10}(r_1, \zeta_1) Y_{1,00}(\vartheta_1, \varphi_1) = -2\zeta_1^{3/2} e^{-\zeta_1 r_1} \frac{1}{\sqrt{4\pi}}$$
$$a(2) = R_{10}(r_2, \zeta_2) Y_{1,00}(\vartheta_2, \varphi_2) = -2\zeta_2^{3/2} e^{-\zeta_2 r_2} \frac{1}{\sqrt{4\pi}}$$

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

$$a(4) = R_{10}(r_4, \zeta_4) Y_{1,00}(\vartheta_4, \varphi_4) = -2\zeta_4^{3/2} e^{-\zeta_4 r_4} \frac{1}{\sqrt{4\pi}}$$

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

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

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

$$b(4) = R_{10}(r_4, \zeta_4) Y_{1,00}(\vartheta_4, \varphi_4) = -2\zeta_4^{3/2} e^{-\zeta_4 r_4} \frac{1}{\sqrt{4\pi}}$$

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

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

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

$$c(4) = R_{20}(r_4, \zeta_4) Y_{1,00}(\vartheta_4, \varphi_4) = -\left(\frac{\zeta_4}{2}\right)^{3/2} (2 - \zeta_4 r_4) e^{-\zeta_4 r_4/2} \frac{1}{\sqrt{4\pi}}$$

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

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

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

$$d(4) = R_{20}(r_4,\zeta_4)Y_{1,00}(\vartheta_4,\varphi_4) = -\left(\frac{\zeta_4}{2}\right)^{3/2}(2-\zeta_4 r_4)e^{-\zeta_4 r_4/2}\frac{1}{\sqrt{4\pi}}$$

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

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

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

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

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

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

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

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

$$-\iiint\iiint\iiint\iiint[a(1)b(2)c(3)d(4)]\frac{1}{2}\frac{d^2}{dr_1^2}[a(1)b(2)c(3)d(4)]d\tau_1d\tau_2d\tau_3d\tau_4$$

$$=-\iiint a(1)\frac{1}{2}\frac{d^2}{dr_1^2}a(1)r_1^2dr_1d\vartheta_1d\varphi_1$$

$$=-\frac{4\zeta_1^7}{2}\int_0^\infty e^{-2\zeta_1 r_1}r_1^2dr_1=-\frac{4\zeta_1^7}{(2\zeta_1)^3}=-\frac{\zeta_1^4}{2}$$

$$-\iiint\iiint\iiint\iiint[a(1)b(2)c(3)d(4)]\frac{1}{r_1}\frac{d}{dr_1}[a(1)b(2)c(3)d(4)]d\tau_1d\tau_2d\tau_3d\tau_4$$

$$-\iiint a(1)\frac{1}{r_1}\frac{d}{dr_1}a(1)r_1^2dr_1d\vartheta_1d\varphi_1=-4\zeta_1^5\int_0^\infty e^{-2\zeta_1 r_1}r_1dr_1=-4\zeta_1^5\frac{1}{(2\zeta_1)^2}$$

$$=\zeta_1^3$$

$$\iiint\iiint\iiint\iiint [a(1)b(2)c(3)d(4)]\frac{\zeta_1}{r_1}[a(1)b(2)c(3)d(4)]d\tau_1 d\tau_2 d\tau_3 d\tau_4$$

$$= \iiint a(1)\frac{\zeta_1}{r_1}a(1)r_1^2 dr_1 d\vartheta_1 d\varphi_1 = \zeta_1 \int_0^\infty e^{-2\zeta_1 r_1}\, r_1 dr_1 = \frac{\zeta_1}{(2\zeta_1)^2} = \frac{1}{4\zeta_1}$$

$$\iiint\iiint\iiint\iiint [a(1)b(2)c(3)d(4)]\frac{l_1(l_1+1)}{2}[a(1)b(2)c(3)d(4)]d\tau_1 d\tau_2 d\tau_3 d\tau_4$$

$$= \iiint a(1)\frac{l_1(l_1+1)}{2r_1^2}a(1)r_1^2 dr_1 d\vartheta_1 d\varphi_1 = \frac{l_1(l_1+1)}{2}\int_0^\infty e^{-2\zeta_1 r_1}\, dr_1$$

$$= \frac{l_1(l_1+1)}{2}\frac{1}{2\zeta_1} = \frac{l_1(l_1+1)}{4\zeta_1}$$

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

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

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

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

$$\iiint\iiint\iiint\iiint [a(1)b(2)c(3)d(4)]\frac{d^2}{dr_3^2}[a(1)b(2)c(3)d(4)]d\tau_1 d\tau_2 d\tau_3 d\tau_4 =$$

$$= \iiint c(3)\frac{d^2}{dr_3^2}c(3)r_3^2 dr_3 d\vartheta_3 d\varphi_3 = \left(\frac{\zeta_3}{2}\right)^3\left(\zeta_3^2 - \frac{\zeta_3^3}{4}\right)\int_0^\infty e^{-\zeta_3 r_3/2}\, r_3^2 dr_3$$

$$= \left(\frac{\zeta_3}{2}\right)^3\left(\zeta_3^2 - \frac{\zeta_3^3}{4}\right)\frac{2!}{\left(\frac{\zeta_3}{2}\right)^3}$$

$$E_{3,KE} = -\left(\frac{\zeta_3}{2}\right)^3 \left(\zeta_3^2 - \frac{\zeta_3^3}{4}\right) \frac{2!}{\left(\frac{\zeta_3}{2}\right)^3}$$

$$- \iiint \iiint \iiint \iiint [a(1)b(2)c(3)d(4)] \frac{d^2}{dr_3^2} [a(1)b(2)c(3)d(4)] d\tau_1 d\tau_2 d\tau_3 d\tau_4$$

$$= -2\left(\zeta_3^2 - \frac{\zeta_3^3}{4}\right)$$

$$- \left[\int_0^\infty \left(\frac{\zeta_3}{2}\right)^{3/2} (2 - \zeta_3 r_3) e^{-\zeta_3 r_3/2} \frac{1}{r_3} \left(\frac{\zeta_3}{2}\right)^{3/2} \left(2\zeta_3 + \frac{\zeta_3^2}{2}\right) e^{-\zeta_3 r_3/2} r_3^2 dr_3\right] - \frac{\zeta_3^2}{2n_3^2}$$

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

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

$$E_{1,EE} = \iiint \iiint \iiint \iiint [a(1)b(2)c(3)d(4)] \frac{1}{r_{12}} [a(1)b(2)c(3)d(4)] d\tau_1 d\tau_2 d\tau_3 d\tau_4$$

$$= \iiint \iiint [a(1)b(2)] \frac{1}{r_{12}} [a(1)b(2)] d\tau_1 d\tau_2$$

$$= \int_0^\infty \int_0^\infty [a(1)b(2)] \frac{1}{r_{12}} [a(1)b(2)] r_1^2 dr_1\, r_2^2 dr_2$$

$$E = \iiint \iiint \iiint \iiint \Psi(\vec{r},\vec{\zeta}) H \Psi(\vec{r},\vec{\zeta})\, r_1^2 dr_1 d\vartheta_1 d\varphi_1 r_2^2 dr_2 d\vartheta_2 d\varphi_2 r_3^2 dr_3 d\vartheta_3 d\varphi_3 r_4^2 dr_4 d\vartheta_4 d\varphi_4$$

$$= \sum_{i=1}^{4}\sum_{j=1}^{4}\sum_{k=1}^{4}\sum_{l=1}^{4}\sum_{m=1}^{4}\sum_{n=0}^{4}\sum_{o=1}^{4}\sum_{p=1}^{4} (ijkl)H(mnop)$$

$$= \sum_{i=1}^{4}\sum_{j=1}^{4}\sum_{k=1}^{4}\sum_{l=1}^{4}\sum_{m=1}^{4}\sum_{n=1}^{4}\sum_{o=1}^{4}\sum_{p=1}^{4} \left[\delta_{im}(i)H_i(m) + \delta_{jn}(j)H_j(n) + \delta_{ko}(k)H_k(o) + \delta_{lp}(l)H_l(p)\right]$$

We define Kronecker's delta function as shown below:

$$\delta_{\mathrm{im}} = \frac{1 \forall \mathrm{i=m}}{0 \forall \mathrm{i \neq m}}$$

$$H_i = -\frac{1}{2}\nabla_i^2 - \frac{4}{r_i} + \sum_{i=1}^{4}\sum_{j=i+1}^{4} \frac{1}{r_{ij}}$$

We use an elitist evolutionary hill climber to compute the zeta values (Slater atomic orbital screening variables). Roulette-wheel selection is utilized. Every generation the zeta values are mutated by constrained random numbers being added to each of the four selected children. We compare our results with the perhaps best theoretical non-relativistic ground-state energy mentioned in the opening paragraph of this research paper.

```
Total Ground-State Energy of Beryllium
Best Theoretical Energy -14.667356508
Atomic Number Z = 4 PRNG Seed = 1
Generations = 100  Population = 25
Number of Steps = 2000000
Zeta 1 Lo = 3.25  Zeta 1 Hi = 4.00
Zeta 2 Lo = 3.25  Zeta 2 Hi = 4.00
Zeta 3 Lo = 3.25  Zeta 3 Hi = 4.00
Zeta 4 Lo = 3.25  Zeta 4 Hi = 4.00

 #  Kinetic     Potential  EE         Total      % Error
 0  -28.643380  -1.072195  15.423573  -14.292002  2.559116
 1  -26.098418  -1.076133  12.878313  -14.296238  2.530232
 2  -28.657531  -1.071892  15.409090  -14.320334  2.365952
 4  -26.127924  -1.076155  12.928894  -14.275185  2.673772
 5  -28.625321  -1.072309  15.249711  -14.447919  1.496097
 6  -26.914596  -1.062470  13.236621  -14.740445  0.498304
 7  -26.125499  -1.076145  11.422315  -15.779329  7.581273
 8  -28.636655  -1.072030  14.338944  -15.369740  4.788753
11  -28.664883  -1.072048  15.057165  -14.679766  0.084605
13  -28.669272  -1.071604  14.603230  -15.137646  3.206367
14  -28.643386  -1.072195  15.231886  -14.483695  1.252176
21  -26.107471  -1.076283  12.722208  -14.461545  1.403195
23  -26.899737  -1.061719  12.960062  -15.001394  2.277420
24  -28.646095  -1.072171  14.369118  -15.349148  4.648362
All energies are in Eh the atomic unit energy

 #  Zeta 1    Zeta 2    Zeta 3    Zeta 4
 0  3.950654  3.883733  3.481955  3.644411
 1  3.650086  3.960454  3.621795  3.655450
 2  3.951654  3.884733  3.484955  3.643411
 4  3.650086  3.962454  3.621795  3.653450
 5  3.948654  3.883733  3.483955  3.642411
 6  3.898765  3.871860  3.872203  3.454787
 7  3.651086  3.961454  3.620795  3.654450
 8  3.950654  3.883733  3.483955  3.644411
11  3.950654  3.885733  3.483955  3.642411
13  3.952654  3.885733  3.485955  3.644411
14  3.950654  3.883733  3.481955  3.644411
21  3.650086  3.960454  3.621795  3.653450
23  3.899765  3.872860  3.875203  3.459787
24  3.949654  3.884733  3.484955  3.641411
Evaluations = 125

Runtime (in Seconds): 7600.901000
```