Variational Solution for the Lithium Like Atom's Schrödinger Equation (Atomic Number Z = 3)

The partial differential equation is as follows:

$$-\frac{h^2}{8\pi^2 m_e}(\nabla_1^2+\nabla_2^2+\nabla_3^2)\psi-\frac{e^2}{4\pi^2\epsilon_0}\left(\frac{Z}{r_1}+\frac{Z}{r_2}+\frac{Z}{r_3}-\frac{1}{|\vec{r}_1-\vec{r}_2|}-\frac{1}{|\vec{r}_1-\vec{r}_3|}-\frac{1}{|\vec{r}_2-\vec{r}_3|}\right)\psi=E\psi$$

This equation can be rewritten in the form using atomic units:

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

Where [1]:

$$\nabla_i^2=\frac{\partial^2}{\partial {x_i}^2}+\frac{\partial^2}{\partial {y_i}^2}+\frac{\partial^2}{\partial {z_i}^2}$$

$$r_i=\sqrt{x_i^2+y_i^2+z_i^2}$$

$$r_{12}=|\vec{r}_1-\vec{r}_2|=\sqrt{(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2}$$

$$\frac{1}{r_{12}}=\frac{1}{r_1}\sum_{l=0}^{\infty}\left(\frac{r_2}{r_1}\right)^l P_l(\cos\theta)\ \forall r_1>r_2$$

$$\frac{1}{r_{12}}=\frac{1}{r_2}\sum_{l=0}^{\infty}\left(\frac{r_1}{r_2}\right)^l P_l(\cos\theta)\ \forall r_1<r_2$$

Let our approximate helium wave function be expressed as follows:

$$\Psi(r_1,r_2,r_3)=\psi_{100}(r_1)\psi_{100}(r_2)\psi_{200}(r_3)$$

$$\psi_{100}(r)=R_{10}(r)Y_{00}(\vartheta,\varphi)=2\zeta^{3/2}e^{-\zeta r}\frac{1}{2\sqrt{\pi}}=\frac{1}{\sqrt{\pi}}\zeta^{3/2}e^{-\zeta r}$$

$$\psi_{200}(r)=R_{20}(r)Y_{00}(\vartheta,\varphi)=2\left(\frac{\zeta}{2}\right)^{3/2}\left(1-\frac{\zeta r}{2}\right)e^{-\zeta r/2}\frac{1}{2\sqrt{\pi}}$$

The radial part of the Laplacian operator is as illustrated below:

$$\nabla_1^2=\frac{1}{r_1^2}\frac{d}{dr_1}\left[r_1^2\frac{d}{dr_1}\right]$$

We compute the derivatives using central differences [2]:

$$\frac{df(\zeta,r)}{dr}=\frac{f(\zeta,r+h)-f(\zeta,r-h)}{2h}$$

$$\frac{d^2f(\zeta,r)}{dr^2}=\frac{f(\zeta h,r-h)-2f(\zeta,r)+f(\zeta,r+h)}{2h}$$

The one-dimensional kinetic energy integrals were computed using Simpson's Rule and limits A = 1.0e-8, B = 18900 and 15000 steps. Again, we utilized Simpson's Rule to calculate the one-dimensional potential energy integrals with limits C = 1.0e-8, D = 9550 and 15000 steps. The electron-electron two-dimensional integrals used the TRICUB function found in [3].

An evolutionary hill-climber of the author's design was used to find a local minimum of the Schrödinger equation.

Results as are to be found as shown below:

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Lithium atom atomic number Z = 3
Experimental ground state energy (au) = -14.9581
Experimental ground state energy (eV) = -407.03
Initial Results:
zeta1 = 3       zeta2 = 3       zeta3 = 3       Z = 3
Electron-electron repulsion energy (au) = 3.5251
Electron-electron repulsion energy (eV) = 95.9227
Kinetic Energy (au) = 9.51036
Kinetic Energy (eV) = 258.789
Potential energy (au) = -27.2933
Potential energy (eV) = -742.686
Total energy (au) = -14.2578
Total energy (eV) = -387.974
% Error = 4.6816
Runtime in seconds = 0.404
Hill Climber Results:
zeta1 = 2.42579 zeta2 = 2.51176 zeta3 = 2.21677 Z = 3
Electron-electron repulsion energy (au) = 2.85095
Electron-electron repulsion energy (eV) = 77.5781
Kinetic Energy (au) = 15.1126
Kinetic Energy (eV) = 411.234
Potential energy (au) = -32.7504
Potential energy (eV) = -891.182
Total energy (au) = -14.7868
Total energy (eV) = -402.369
% Error = 1.14496
Runtime in seconds = 33.872
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References

[1] L. I. Schiff, Quantum Mechanics Third Edition, New York: McGraw-Hill Book Company, 1968.

[2] S. D. d. B. C. Conte, Elementary Numerical Analysis Third Edition, New York: McGraw-Hill Book Company, 1980.

[3] H. T. Lau, A Numerical Library in C for Scientists and Engineers, Boca Raton: CRC Press, 1994.