

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

The partial differential equation is as follows:

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

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]:

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

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

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

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

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

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]:

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

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

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 = 0.413
Hill Climber Results:
zeta1 = 2.38881 zeta2 = 2.61348 zeta3 = 2.36409 Z = 3
Electron-electron repulsion energy (au) = 2.93547
Electron-electron repulsion energy (eV) = 79.8779
Kinetic Energy (au) = 14.4711
Kinetic Energy (eV) = 393.777
Potential energy (au) = -32.3176
Potential energy (eV) = -879.404
Total energy (au) = -14.911
Total energy (eV) = -405.748
% Error = 0.314818
Runtime in seconds = 1240.5
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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.